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**BASIC STUDIES ON RADIATION ENERGY TRANSFER
MECHANISMS OF CHEMICAL SYSTEMS**

Task 9R47-16-010-02, HT H-1

Contract DA 44-177-TC-725

December 1962

prepared by:

DENVER RESEARCH INSTITUTE
University of Denver
Denver, Colorado



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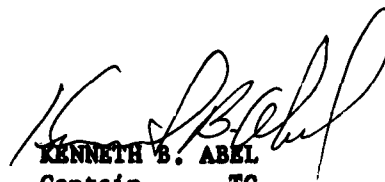
**HEADQUARTERS
U. S. ARMY TRANSPORTATION RESEARCH COMMAND
Fort Eustis, Virginia**

**This report reviews and summarizes the work performed under Contract
DA 44-177-TC-725 for the U. S. Army Transportation Research Command.**

**Work on this project was carried out by the Denver Research Institute,
University of Denver, Denver, Colorado during the period June 1961
to June 1962. Mr. George E. Bohner was the principal investigator.**

**The conclusions and recommendations contained in the report are con-
curred in by this command.**

FOR THE COMMANDER:


**KENNETH B. ABEL
Captain, TC
Adjutant**

APPROVED BY:


**JAMES P. WALLER
USATRECOM Project Engineer**

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TCREC Technical Report 62-90

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Prepared by
Denver Research Institute
University of Denver
Denver 10, Colorado

for
U. S. ARMY TRANSPORTATION RESEARCH COMMAND
FORT EUSTIS, VIRGINIA

Report prepared by George E. Bohner, Project Supervisor

FOREWORD

This report was prepared under Contract DA 44-177-TC-725 for the U. S. Army Transportation Research Command, with Mr. James Waller acting as the representative of the contracting officer.

The report covers the work conducted from 1 June 1961 to 31 August 1962. The work was conducted under the technical administration of Dr. J. J. Schmidt-Collerus, with Mr. George E. Bohner acting as principal investigator and project supervisor. The author wishes to acknowledge the assistance of Mr. F. S. Bonomo in much of the spectroscopy work.

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SUMMARY

This research was undertaken in order to gain information that would lead to a better understanding of how some organic compounds are able to protect others from degradation while under the influence of high-energy irradiation. Cyclohexane was chosen as the solvent to be studied, with benzene, biphenyl, and naphthalene being the principal "protecting" additives. By identifying the various products formed in these solutions and determining the influence of dose and additive concentration on the rate of formation of the products, certain conclusions regarding the radiolytic degradation mechanisms can be made. The formation and subsequent reactions of radiolytically formed free radicals cause most of the degradation observed in pure cyclohexane. When an aromatic additive is present, it reacts with these radicals and competes with the normal degradation reactions. As a result, the additive disappears from solution at a rather rapid rate to form a small amount of rather simple compounds. The greater part of the reacted additive is found in the radiation-produced polymer. Each additive molecule appears to react with more than one free radical. The reaction of the additive with the free radicals results in a decrease in rate of formation of the products derived from the radiolysis of pure cyclohexane.

Almost all the experimental results can be explained in terms of free radical mechanisms. A reaction degradation scheme is proposed which is consistent with the experimental results.

INTRODUCTION

In recent years much of the interest in radiation chemistry has been concerned with determining the stability of certain compounds or classes of compounds toward radiolytic degradation. Studies have been confined primarily to determining the effects of radiation on the physical properties of the materials. Other studies identified the types of products formed and attempted to define the mechanisms for their formation.

One area of particular interest is derived from the observation that certain compounds in very small quantity are able to protect another compound from much of its normal radiolytic degradation. Specifically, a small amount of benzene, present in cyclohexane, reduces the amount of hydrogen formed by radiation by a much greater amount than expected. Benzene is thus said to have a protective effect on the degradation of the cyclohexane. This phenomenon has been termed "energy transfer", which is derived from the hypothesis that energy absorbed by the cyclohexane, normally causing its degradation, is transferred to the more radiolytically stable benzene, which then dissipates the energy via processes which result in no apparent degradation of the benzene. This mechanism of energy transfer is based almost entirely on observations and conclusions derived from the formation of hydrogen by the radiolysis of solutions of cyclohexane containing varying amounts of benzene.

The object of the present research program is to obtain more information regarding the mechanisms by which benzene protects cyclohexane during irradiation. To accomplish this goal, we proposed that the identification and the measurement of the rates of formation of the major products derived from the radiolysis of the cyclohexane-benzene system would provide a means of more clearly elucidating the radiolytic degradation mechanisms and might provide a way for ascertaining the importance of the role of energy transfer if such actually exists. The determination of the mode of protection in a relatively simple system such as benzene and cyclohexane, aside from being a contribution to the basic knowledge of radiation chemistry, can aid in the development of more complicated systems where maximum radiation stability is desired.

PRESENT CONCEPTS REGARDING THE RADIATION CHEMISTRY OF ORGANIC COMPOUNDS

The literature on the radiation chemistry of organic compounds contains several comprehensive reviews^{20, 34, 48, 52}. This discussion is intended to provide a general background from which a better understanding of the reported research work can be derived.

The objective of radiation chemistry is to define the processes that cause observable changes when a material is subjected to the influence of radiation. Current concepts narrow the field of radiation chemistry to the study of processes resulting from high-energy electromagnetic radiations and exclude many of the concepts of photochemistry. Often the latter exclusion is justified; however, it would be rather difficult to stipulate at what energy of radiation the concepts of photochemistry cease to apply to the present concepts of radiation chemistry.

Electromagnetic radiations below a wave length of about 100 Å are called X-rays or gamma rays depending upon their origin. The energy of these radiations when passing through matter can be dissipated in three primary ways; namely, pair production, Compton scattering, and photoelectric absorption. These processes are briefly defined below:

- a. Pair production is the process by which a photon forms an electron and a positive particle (positron). For this process to occur, the incident photon must possess at least 1.02 Mev. of energy. If pair production occurs, the energetic electron and positron lose their energy by causing ionization and excitation. The positron is destroyed by combination with an electron to give two photons with an energy of 0.5 Mev. The latter is designated as annihilation radiation.
- b. Compton scattering occurs when photons lose part of their energy by inelastic collisions with electrons from atoms. The ejected electrons cause ionization and excitation while the scattered photon, though of reduced energy, undergoes further Compton scattering and energy

reduction by photoelectric absorption. Compton scattering is of primary importance when gamma rays interact with materials of low atomic number. When these gamma rays possess energy in excess of 1 Mev., almost all of the ejected electrons result from Compton scattering.

c. Photoelectric absorption is the process whereby the incident photon is absorbed by an atom and a fast electron is ejected. This absorption is greatest for radiation of low energy interacting with material of high atomic number.

The above processes are of primary interest to the physicist. The chemist is interested in the results of these physical processes. Under the influence of high-energy radiation, sufficient energy is available to cause the excitation or ionization of any electron in the molecule. In aromatic liquids, ionization presumably can occur but cannot be measured accurately. Such ions, if formed, seem to be neutralized to yield the parent molecule in an excited state⁴¹. The effects of radiation on aromatic molecules, therefore, appear to result from the action of excited molecules. The excitation affects the entire molecule, and if a reaction is to occur it may or may not take place in the track of the incident particle. In aliphatic liquids, the excitation may affect the entire molecule; but here the lack of resonance results in a less stable molecule, which often is exemplified by preferential bond breaking.

The chemical effects produced in liquids during radiolysis may be initiated by two differently excited species¹³. One, formed in the primary ionization process, usually is in its lowest excited state and can diffuse away from the point of formation either as an excited or a deactivated molecule. Deactivation occurs through photon emission or dissociation into a free radical, the latter resulting in a chemical reaction. The other, formed through a charge neutralization process, is in a much higher energy state than the one formed by direct excitation and decomposes rapidly into radicals before leaving its point of origin.

The excitation energy can be transferred from one molecule to another. The mode of energy transfer is controversial and any one or all of the transfer mechanisms listed below may contribute in a particular system⁴⁸. This transfer of energy* may occur by (a) simple collision, (b) emission of a photon which is absorbed by another molecule, (c) inductive resonance, or (d) excitation transfer.

Excited molecules, whether formed by energy transfer or by primary radiation, can lose energy by fluorescence or internal conversions to give strongly vibrating lower electronic states. The vibrational energy can be lost by collisions. The excited species can decompose to yield molecular products by a unimolecular process or by reaction with other excited species. Decomposition to form free radicals is also possible.

The formation of free radicals and their subsequent reactions provide a means of accounting for many of the products formed during the radiolysis of organic liquids. Since free-radical mechanisms can account for many of the products formed in the condensed state, it is logical to assume that the actual rate of radical formation is much greater than that indicated by any of the methods used for the detection of free radicals. The highly reactive radicals can recombine within the solvent cage (environment of immediate reaction), thus leading to no observable reaction. This is known as the Franck-Rabinowitch effect. The more energetic and less reactive radicals can escape from the cage and thus can enter into observed reactions.

In the rigid structure of the solid state, the Franck-Rabinowitch effect is reduced and the identification and quantitative measurement of free-radical formation is possible with electron spin resonance techniques and ultraviolet absorption

* Energy transfer should not be confused with the term "Linear Energy Transfer", or LET, which is used frequently in describing the linear density of events occurring in a radiation track. LET effects need not be considered here since they are dependent upon the type of radiation, but LET does affect the amount and type of yield products found in the radiolysis of organic compounds³⁰.

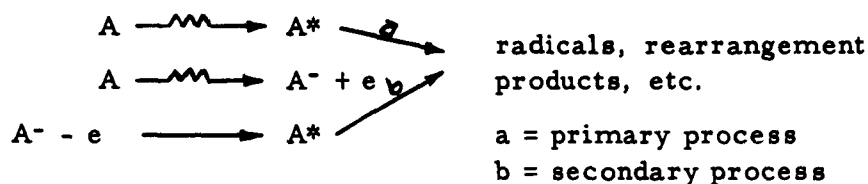
spectroscopy. The Franck-Rabinowitch effect is more operative in the liquid state, thus making it impossible to measure the total degree of radical formation by these or other methods; however, methods are available whereby the radicals escaping from the solvent cage can be detected and quantitatively measured. These methods utilize either the effects of the radicals formed on the polymerization of certain monomers or the radical-combination reactions of such materials as diphenylpicrylhydrazyl (DPPH) or iodine and are known as radical-scavenger techniques.

The chemistry of many free-radical reactions is quite well understood. Many radiation-produced radicals can, however, possess excess energy ("hot radicals") which results in a high energy of activation. These radicals can undergo reactions which normally do not occur. Also, the radiation-produced radicals can be formed in high concentrations in localized areas along the radiation track. This can result in product distributions considerably different from those expected in normal radical reactions.

Since analytical techniques are unable to distinguish between products formed from "hot radicals" and the products formed from "normal radicals" and also between those formed in localized high-concentration areas and those formed in more diffused radical-concentration areas, specific reaction rate constants derived from the analysis of products produced by an irradiation may or may not provide information regarding the actual radiolysis mechanisms. Such information would be enlightening as far as the overall degradation mechanism rates are concerned; however, it would leave completely obscure any detailed description of intermediate processes that occur. Any mechanism derived solely from kinetic considerations could very easily lead to erroneous mechanistic conclusions. Therefore, the most logical approach for ascertaining the mechanisms responsible for the observed chemical changes in an organic system is the nonkinetic approach combined with certain thermodynamic and kinetic considerations such as bond energies, radical reactivities, and parameters which affect the nature of the radiation environment, i. e., dose, dose rate, LET, temperature, etc.

Wherever possible, a postulated reaction mechanism should be investigated independently of the radiation environment.

Before proceeding further into some aspects of free-radical behavior and radiation kinetics, a brief summation of the foregoing discussion is in order. Radiation energy absorbed by an organic system results in the formation of excited molecules and free radicals which are responsible for the production of many of the yield products. These can result from bond scissions, molecular rearrangement (or reactions involving the excited molecules and radical combination), radical attack reactions, or radical induced chain reactions of the radiolytically produced free radicals. The formation of the initial reactive species can be depicted by the following reactions:



An electron produced by Compton scattering from 1 Mev. photon can result in the excitation of more than 30,000 molecules⁴³. The energy of the 1 Mev. photon is in the order of 23×10^6 kcal./mole, which is far in excess of chemical bond energies. These figures show that for Co^{60} gamma photons, which have energies of 1.17 and 1.33 Mev., if all the radiation energy were absorbed, very much damage to a molecule would result. Complete energy absorption does not occur and much of the energy absorbed by the molecule is dissipated by various processes without damage.

Free-radical reactions play important roles in many types of chemical reactions. The bond-fission responsible for radical formation (homolytic cleavage) can be depicted as $A:B \longrightarrow A^\cdot + B^\cdot$ and is distinguished from heterolytic cleavage, $A:B \longrightarrow A^- + B^+$. Energetically, homolytic cleavage should be favored over heterolytic cleavage. Often, however, solvent effects tend to promote the latter⁵³. Generally, there are two classes of organic free radicals:

- (a) those stabilized by resonance which possess a relatively long life, such as triarylmethyls, and
- (b) those not or only partially stabilized by resonance which are short lived, such as phenyl and methyl.

After a radical is formed in solution, it can react in various ways depending upon the activity of the radical and the sensitivity of the solvent toward radical attack⁵⁰. As seen in Table I, the sensitivity of various aromatic compounds toward phenyl-radical attack varies considerably. Perhaps the variation in activity of various aromatic compounds toward reaction with the phenyl radical can be considered in a reverse manner when the solvent from which the free radicals are derived by irradiation is aliphatic rather than aromatic. This suggestion would lead to the postulation that various aromatic solutes in an aliphatic solvent would exert their effects by varying reactivities toward the radicals produced. This is to say that a solute which is highly reactive with free radicals would show a more pronounced effect in a particular system than would a solute of lesser activity. In other words, naphthalene (see Table I) might be expected to exert a greater influence on the radiolytic degradation of cyclohexane than would benzene.

TABLE I
RELATIVE REACTIVITY AND ISOMER DISTRIBUTION FOR THE
REACTION OF SOME AROMATIC COMPOUNDS WITH PHENYL
RADICALS DERIVED FROM BENZOYL PEROXIDE

Compound	Relative Reactivity	Isomer Distribution			Ref.
		% ortho	% meta	% para	
Benzene	1.00	---	---	---	
Anisole	1.2	67	18	15	2, 3
Toluene	1.9	71	17	12	36
Ethylbenzene	---	50	25	25	4
Biphenyl	4	48.5	23	28.5	17
Naphthalene	23.9	---	---	---	35

If, during irradiation, chemical bonds are to be broken, the weakest bonds should be broken first and at a faster rate. This is observed indeed in the radiolysis of aliphatic hydrocarbons. For aromatic hydrocarbons, however, the effects of bond-energy differences are not so pronounced. If an aromatic molecule contains bonds other than C-C and C-H, then the energy of these bonds may be of significance in the radiolysis degradation mechanisms. Since hydrocarbons possess only carbon-carbon and carbon-hydrogen bonds, the study of the radiolytic decomposition of these compounds is easier than that of compounds containing a greater variety of bond groupings. Since all the C-C and all the C-H bonds in cyclohexane are equivalent, the study of this compound is simpler than that of a corresponding open-chain compound where two different types of C-H bonds are present. This is one of the basic reasons why the radiolysis of cyclohexane has received so much study. A similar situation exists for benzene.

Since the primary object of this research program was to study the mechanisms occurring in the radiolysis of cyclohexane solutions containing solutes capable of protecting the cyclohexane from radiolytic damage, a review of prior work is presented in the following paragraphs.

The radiolysis of cyclohexane produces hydrogen, cyclohexene, bicyclohexyl, a cyclohexylhexene, and polymer as the main products. The yield values listed in Table II are a reasonable average for most of the data reported in the literature.

TABLE II
YIELD VALUES OF THE MAIN PRODUCTS PRODUCED
BY GAMMA IRRADIATION OF CYCLOHEXANE

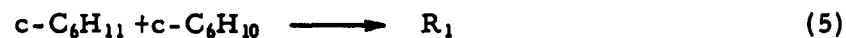
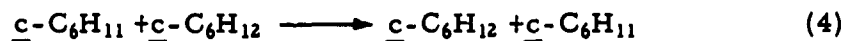
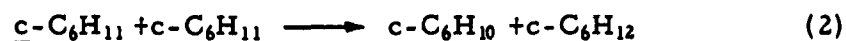
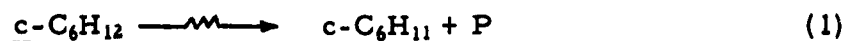
Product	G Value
Hydrogen	5.0 - 5.8
Cyclohexene	3.3 - 1.8
Bicyclohexyl	1.95 - 1.2
Cyclohexylhexene*	.27 - .23
Polymer	1.7 - 3.9

*The identification of this component is questionable; it may be a cyclohexylcyclohexene or possibly cyclohexylhexane. Dyne and Stone²⁵ suggest that it is cyclohexylhexene-1.

There is considerable variability in many of the values reported. Some of the variation can be attributed to differences in analytical techniques, dosimetry errors, and sample size and geometry; but most is probably due to total dose and dose rate. The yields of hydrogen, cyclohexene, and bicyclohexyl are reduced at relatively high doses²⁹. The decrease in hydrogen with increasing dose probably is due to the accumulation of olefinic products which can scavenge hydrogen atoms and also may offer some protection to the cyclohexane through some kind of energy transfer mechanism. Conversely, the apparent decrease in cyclohexene yield may be due to its reaction with the hydrogen atoms to reform cyclohexane and/or other products. The decrease in yield of other products is probably altered by secondary reactions.

Barker and Hill⁵ have shown that the rate of polymer formation from cyclohexane radiolysis increases with increasing dose up to a dose of about 15×10^{20} ev. per gram. At doses greater than this, the polymer yield remains almost constant at a value of about 2.5. They indicate that the polymer is a secondary product which consists of a complex mixture of six-membered ring hydrocarbons, the molecular weight of which increases with dose.

Probably the formation of liquid products in the radiolysis of cyclohexane can be explained by the following reactions:



Reaction (1) is the initial reaction which forms the cyclohexyl radical and a product P (probably hydrogen) which will be discussed later. Reaction (2) is a disproportionation which forms cyclohexene and cyclohexane from two cyclohexyl radicals. Reaction (3) forms bicyclohexyl from the combination of two cyclohexyl radicals. Reaction (4) can be considered a radical formation reaction whereby cyclohexyl radicals are formed from radical reaction rather than by the direct effects of radiation. This would be a secondary reaction but the results of the radicals' formation are indistinguishable from the primary radical formation reactions. Reaction (5) results in the formation of a new radical, R_1 , which can react with other molecules or radicals in the solution to form other radicals as in (6) or products. These reactions (5 and 6) result in the formation of polymer.

Based on the initial yields of cyclohexene and bicyclohexyl from Dyne's work²⁵, a composite value of $G = 7.2$ expressed as cyclohexane molecules converted to product is obtained. This represents the products of reactions (2) and (3). The combined yields of the dimer and polymer from Barker's work⁵ give a G value of 3.9, which is about half the total decomposition of the cyclohexane. Barker postulates that this yield reduction is attributed to the cyclohexene's acting as a quencher for excited cyclohexane molecules and that there is very little decomposition of the cyclohexene molecules. The stability of cyclohexene, however, can be questioned since it is known to form rather large amounts of polymer, $G(\text{polymer}) = 8 - 12.5^{28, 42}$, and other products. Dyne and Fletcher²³ in their studies of cyclohexane-cyclohexene solutions conclude that cyclohexene acts as a radical scavenger rather than by quenching activated species.

There is considerable evidence which indicates that there are two distinct activated species formed in the radiolysis of cyclohexane which are responsible for forming the observed products^{28, 29}. One of these species is subject to "protection" by benzene and has a G value of 3. The other has a G value of 2.4 and is not "protected" by benzene. More discussion of these species will be made in a later section.

The mode of hydrogen formation in the radiolysis of cyclohexane (reaction 1) has been studied in detail. Most of these studies have been made from solutions containing various solutes where most of the solutes are considered to be radical scavengers or in some cases "protectors". This discussion, aside from reviewing some of the current aspects of hydrogen formation, will serve as an introduction to free-radical mechanisms and various solute effects in the radiolysis of cyclohexane solutions.

As previously mentioned, the formation of hydrogen from the radiolysis of cyclohexane gives $G(H_2)$ values ranging from 5.0 to 5.8. Some reported values are lower than 5; however, most values appear to be grouped around a value of 5.4, which is generally considered to be the initial yield of the radiolytically formed hydrogen.

In the radiolysis of mixtures of cyclohexane and benzene, a decrease in hydrogen yield below that indicated by a law of averages is observed (see Figure 1). This is attributed to a protective effect of the "sponge"-type by the benzene^{42, 10}. Apparently two types of hydrogen are formed, i. e., molecular and atomic. Hydrogen atoms are readily converted to HI by the addition of iodine. The indicated yield of H-atoms as shown by the reduction in total hydrogen yield by the presence of iodine is slightly greater than 2^{14, 15}. The remainder of the total hydrogen, ≥ 3.5 , is molecular hydrogen and its formation is not affected by the presence of iodine. These values represent the first attempts to determine the origin of hydrogen from the radiolysis of cyclohexane. There still appears to be considerable controversy on the subject. Molecular hydrogen may be formed from a single-step reaction and is a unimolecular process as indicated in reaction 7.

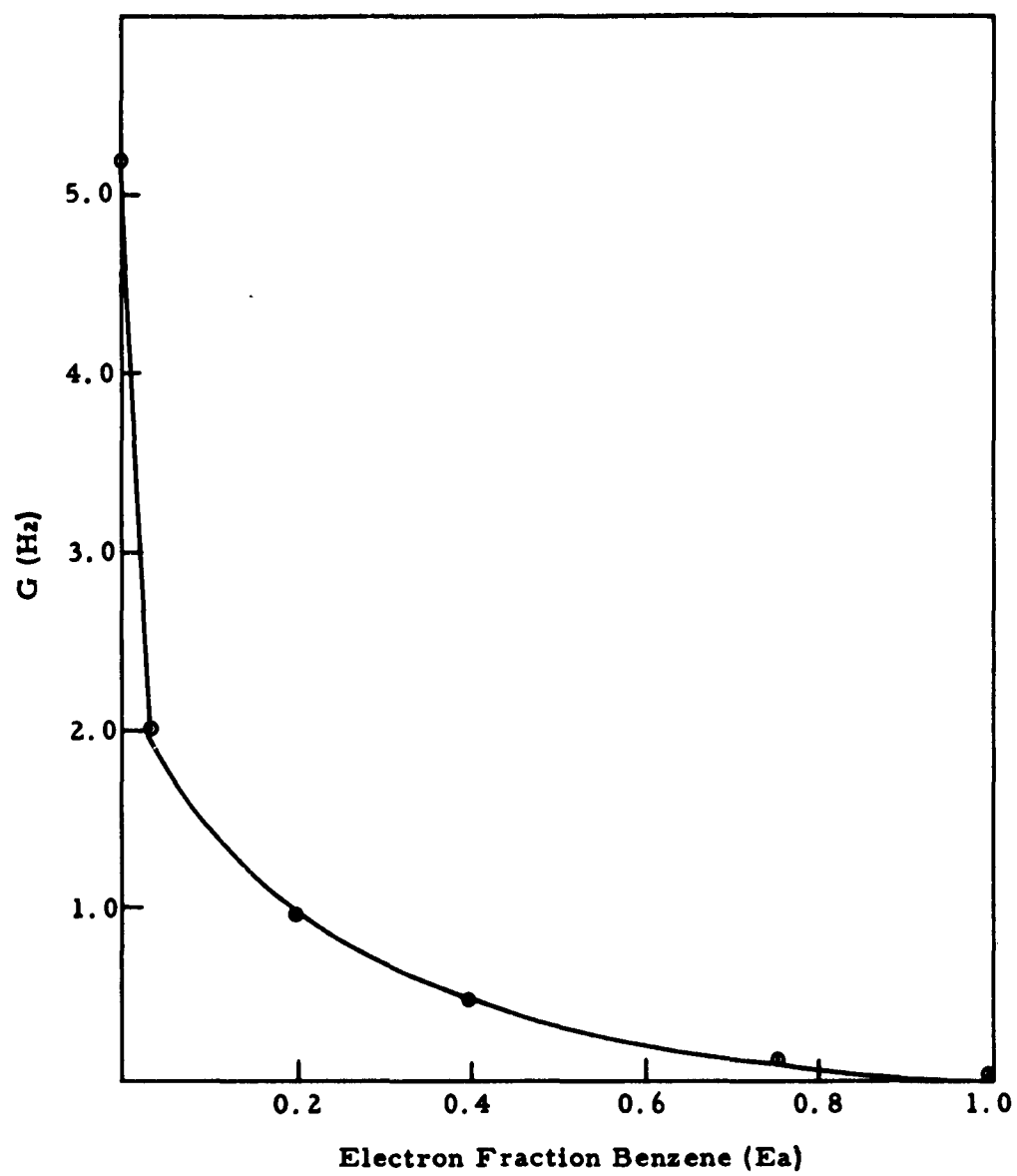
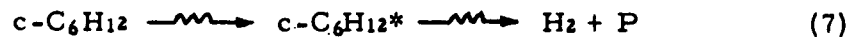


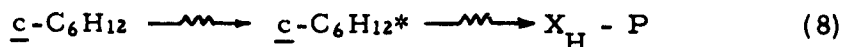
Figure 1. Relation of Hydrogen Yield to Benzene Concentration.



P = other products

* = activated species

Atomic hydrogen is formed via a bimolecular process as shown in reactions 8 and 9.



X_H = reactive species

Dyne and Jenkinson²⁴, using mixtures of $\underline{\text{c}}\text{-C}_6\text{D}_{12}$ - $\underline{\text{c}}\text{-C}_6\text{H}_{12}$ and measuring the D_2 yield, have determined that the unimolecular yield (reaction 7) from $\underline{\text{c}}\text{-C}_6\text{D}_{12}$ is 0.25. They postulate that the corresponding yield of H_2 from $\underline{\text{c}}\text{-C}_6\text{H}_{12}$ will be considerably higher and is very probably in the range of 0.5 - 1.0. A molecular hydrogen yield value of 0.7 is reasonable in view of the observation of Dewhurst²¹ that cyclohexene attains a constant, steady-state yield of 0.7 and cyclohexene is the most probable product to be derived from a unimolecular process. The presence of iodine reduces the unimolecular yield by only about 10%, whereas biphenyl reduces the yield by 50%²⁴. If the unimolecular mechanism is as is indicated by reaction 7, then the biphenyl must quench the activated species²⁴. This is taken to indicate an example of the energy-transfer process postulated by Manion and Burton^{42*}. The main conclusion made by Dyne is that molecular hydrogen formed via a unimolecular process is a small fraction of the total hydrogen, i.e., 10-20%, and is in contradiction to the results of Burton et al.¹⁴. If the balance of hydrogen comes from two processes (as in Burton's conclusions), then both these processes must be bimolecular.

* Author's Note - It seems that this conclusion of an energy transfer process is made without sufficient evidence. If biphenyl quenches the precursor which forms the molecular hydrogen (unimolecular process) at a rate fivefold greater than iodine and if the radiolytic cyclohexene is derived from the unimolecular process, then the reduction in cyclohexene yield should be reduced by fivefold in biphenyl solutions as compared to iodine solutions. This is not known. Also, the relative reactivity of various solutes with hydrogen atoms can be quite different. If biphenyl is more reactive toward hydrogen atoms than iodine, then the observed results could be explained via this means without invoking any energy transfer mechanisms.

Further work by Forrestal and Hamill²⁷ using iodine as a scavenger shows that cyclohexene is formed with an average $G(C_6H_{10}) = 1.9$. The $G(C_6H_{10}) = 0.8$ reported by Dewhurst²¹ is indicated by Forrestal to be in error due to analytical procedures. This represents a $G(C_6H_{10}) = 2.6 - 1.9 = 0.7$, while $G(H_2) = 5.9 - 3.9 = 2$ is the hydrogen yield decrease. Forrestal uses these values to derive an expected $G(C_6H_{10}) = 3$ which is not observed and proposes the contention that a cyclohexadiene formed by radiolysis is responsible for the difference in the observed and theoretically expected cyclohexene yields when theory is based on the formation of hydrogen alone.

Hardwick³² has presented data which, though not intended to explain the above discrepancy, may offer some clue for its existence. About 18% of the hydrogen atoms reacting with cyclohexene do so by hydrogen abstraction; the remainder, by addition to the double bond. If this is the case, then much of the cyclohexene which is formed by radiolysis of cyclohexane would be converted by hydrogen atom addition back to cyclohexane and would thus be undetected in a determination of cyclohexene.

In brief summary, it appears that the mode of hydrogen formation in the radiolysis of cyclohexane is not completely understood. It seems quite definite that the observed hydrogen yield is derived from at least two types of reaction. Whether the precursors to these reactions are identical or different cannot be stated definitely. The hydrogen yields from these reactions can be affected to varying degrees by the presence of compounds that possess different reactivities toward the hydrogen species. A bit of evidence that might be in support of a common precursor for these species is seen in the work of Burrell⁹, who, from Electron Paramagnetic Resonance studies of irradiated cyclohexane, shows that the cyclohexyl radical is predominant (> 95%) in the irradiated compound.

In Table III are listed some relative reactivities of hydrogen atoms with some aromatic compounds. Although these data are not directly related to the present discussion, they have a somewhat direct bearing on the subsequently reported research.

TABLE III
THE RELATIVE REACTIVITY OF HYDROGEN ATOMS
WITH AROMATIC SOLVENTS

	Relative Reactivity ^{a, b}
Benzene	1
Biphenyl	7.5
Naphthalene	8.1
<u>o</u> -Terphenyl	11.0
<u>m</u> -Terphenyl	11.0
<u>p</u> -Terphenyl	20.5
Anthracene	17.3
Diphenylpicrylhydrazyl	57.0
^a Benzene = 1. ^b reference 33	

The radiation stability of benzene and other aromatic hydrocarbons is about ten times greater in the liquid phase than similar aliphatic hydrocarbons. The reason for this increased stability is that the excitation energy must be associated with the electrons in the nonlocalized π orbitals so that insufficient energy can accumulate in any one vibrational mode to lead to decomposition and is generally considered resonance stabilization. The main products derived from the radiolysis of benzene are shown in Table IV.

TABLE IV
YIELD VALUES OF THE MAIN PRODUCTS PRODUCED BY
THE GAMMA IRRADIATION OF BENZENE

Product	G Values
Hydrogen	0.06 - 0.08
Acetylene	0.01 - 0.04
Biphenyl	0.04 - 0.08
Polymer	0.8 - 1.4

The molecular weight of the polymer, ranging from 250-430, appears to be a function of the absorbed dose⁴⁴. The major part of the polymer consists of terphenyls, partially hydrogenated terphenyls, and other products of considerably higher molecular weight. The polymer appears to be formed via free-radical mechanisms. In fact, all the products with the exception of acetylene appear to be derived from the action of free radicals.

The ability of benzene or other aromatic compounds to dissipate absorbed energy without decomposition or their susceptibility to attack by free radicals seems to be very closely associated with the phenomenon of "protection" when these compounds are present in small quantities in solvents that are not so stable to radiation. The action of aromatic compounds in such solvents as cyclohexane has been utilized to gain information regarding the mechanism of hydrogen formation, but there has been much less work done with regard to the effects of aromatic solutes on the nongaseous yield products derived from the radiolysis of the aliphatic hydrocarbon solvents. Some recent work reported by Freeman²⁹, Burr, Strong, and Goodspeed⁹, and Gaumann³¹ represents the first attempts to relate the entire range of radiolytic product yields to the degradation mechanisms occurring in solutions. Lamborn and Swallow³⁹ have studied the relation of hydrogen formation to polymer formation in the cyclohexane-benzene system. Some other studies which have a direct bearing on the following discussion are those of Adams, Baxendale, and Sedgwick¹, Prevost-Bernas, Chapiro, Cousin, Landler, and Magat⁴⁵, MacLachlan⁴⁰, Hughes and Garrison³⁷, Hughes³⁸, Charlesby and Lloyd¹⁸, and Charlesby, Davison, and Lloyd¹⁹. These studies basically utilize various free-radical scavengers to arrive at the proposed degradation mechanisms. Burton, Berry, and Lipsky¹² and Burton, Ghosh, and Yguerabide¹⁶ report work utilizing induced luminescence to show evidence of energy transfer.

Burr et al.⁹ have shown that benzene disappears from cyclohexane solutions at a rate much faster than would be expected if it is functioning solely as an energy absorber for energy absorbed by the cyclohexane. Benzene disappears in such a manner that $1/G(-\text{benzene})$ is a linear function of total dose. Kinetically, this represents a competition between

benzene and some other radiolysis product, probably cyclohexene, for the radiation-produced radicals. Benzene is suggested to be a highly efficient scavenger and has the ability to scavenge several radicals for each benzene molecule disappearing from solution. Phenylcyclohexane is identified as one of the products derived from the reaction of benzene and cyclohexane during radiolysis. Freeman²⁹ unfortunately did not identify this product as phenylcyclohexane, and consequently his suggested mechanisms differ somewhat from those proposed by Burr. The product identification by Burr is supported by the work of Gaumann³¹ and the work of this research (see later sections). The work of both Burr and Gaumann suggests that the transfer of energy between cyclohexane and benzene is much less important in the role of "protection" than many workers in the field believe.

Gaumann³¹ gives data related to the formation of polymer (products of molecular weight greater than the dimer). The polymer yield, though quite variable, does not show any particular dependence on the benzene concentration. With benzene concentrations ranging from 10 to 80%, the G polymer is about 1.35. Lamborn³⁹, on the other hand, shows a very significant dependence of polymer formation on benzene concentration; i. e., the rate of polymer formation decreases rapidly with increasing benzene concentration. Based on the experimental techniques used, it appears that the benzene concentration dependency observed by Lamborn is due entirely to the decrease in yield of bicyclohexyl (a dimer), which is known to be dependent upon the benzene concentration^{29, 31}. Lamborn and Swallow³⁹ conclude "that the protective action of benzene is due to its preferentially taking up the energy of the fast electrons rather than to an initially random absorption of energy followed by some form of 'energy transfer' from cyclohexane to benzene." It should be noted that this conclusion regarding energy transfer is basically the same as that of the previous paragraph even though the reaction mechanisms invoked to arrive at the conclusions are very different. It is suggested that the former conclusion (radical scavenging) is more plausible since this mechanism can readily account for the formation of such products as phenylcyclohexane in the irradiated solutions. Preferential energy absorption by the benzene would infer that benzene, as a pure compound, would absorb more energy from a given irradiation dose than would cyclohexane. This is not an accepted axiom in the field of radiation chemistry.

MacLachlan⁴⁰, using benzyl chloride as a free-radical scavenger, found in cyclohexane solution an indicated radical yield of $3.9 = G(-C_6H_5CH_2Cl)$. For the products derived from the decomposition of the solute, he found a total G radical value of 1.79, or 46% of the total reacted benzyl chloride. The above G $(-C_6H_5CH_2Cl) = 3.9$, when calculated in terms of energy absorbed only by the benzyl chloride, i. e., electron fraction, is 325. "Assuming reaction to occur only through carbon-chlorine bond rupture it can be calculated that 0.3 ev. of energy is expended per bond rupture." The bond strength is 3.5 ev. According to MacLachlan, "This implies, that either benzyl chloride has received energy by transfer from excited cyclohexane or some other process is responsible for its reactivity." The assumption that reaction occurs only at the C-Cl bond may not be justified, as compounds similar to benzyl chloride have been shown to possess considerable variation in reactivity toward hydrogen atoms⁷. Also, the remaining 54% of "unidentified benzyl chloride" products may be found in polymer residues. This work is not a clear point in favor of energy transfer processes and could very probably be interpreted to favor radical scavenger mechanisms as the "protective" mechanism.

Adams et al.¹ used *p*-benzoquinone as a radical scavenger in cyclohexane to arrive at results regarding hydrogen formation similar to those obtained using iodine as a scavenger (see previous discussions). Waight and Walker⁴⁹ used the benzoquinone as a scavenger and observed that the decrease in hydrogen paralleled the decrease in bicyclohexyl. The presence of benzoquinone had very little effect on the formation of cyclohexene, which would indicate that if cyclohexene is formed from the process from which molecular hydrogen is derived, i. e., reaction 7, then bicyclohexyl, which is affected by benzoquinone, must be formed from a process involving the reactive species of reactions 8 and 9. There is very little polymeric material of high molecular weight formed when benzoquinone is present in the solution⁴⁹. This compound is known to be an efficient inhibitor of free-radical-induced chain polymerization reactions. The absence of high-molecular-weight polymer formation with benzoquinone present is evidence to exclude any significant contribution of ionic mechanisms to the degradation process.

A number of other free-radical scavengers have been used to determine the rate of free-radical formation. Diphenylpicrylhydrazyl (DPPH) has been used quite extensively and, in general, gives satisfactory results. Its solubility in aliphatic hydrocarbons is low, which is one of the major disadvantages of using this compound. In aerated cyclohexane, DPPH gives $G(-DPPH) = G(\text{radical}) = 11.7$; for benzene the value is 0.8^{45} . Iodine cyanide has been used as a radical scavenger to a very limited extent in studying the radiolysis of pure compounds such as benzene and cyclohexane^{37, 38}. In benzene the rate of radical formation is quite dependent upon the initial concentration of the scavenger, ranging from $G(\text{radical}) = 2.6$ at $3.6 \times 10^{-2} M$ ICN to $G(\text{radical}) = 0.42$ at $5 \times 10^{-4} M$ ICN. Based on these results, it appears that the degree of radiation stability of benzene as measured by radical formation is dependent upon the nature of the scavenger used. The rate of radical formation in cyclohexane using ICN as an indicator is concentration dependent, with $G(\text{radical})$ approaching 4 at $1.1 \times 10^{-2} M$ ICN. These results are significant only to show that any interpretation made from radical scavenger studies must be made with caution, as the observed results may be influenced by the nature of the scavenger, its concentration, or its mode of reaction. Careful selection of the scavenger to be used must be made since different scavengers can react in different ways. As an example, iodine seems to be ideal when aliphatic hydrocarbons are to be studied; however, when aromatic hydrocarbons are to be studied, the conclusions become much more complicated, probably as the result of the solvent itself acting as a scavenger^{47, 26}.

Charlesby et al.^{18, 19} have used anthracene to study the free-radical mechanisms in cyclohexane. Their results indicate a $G(\text{radical})$ of about 6 and conclude that there is no evidence for energy transfer mechanisms in this system.

Burton et al.^{12, 16} have studied luminescence of cyclohexane solutions containing small amounts of benzene and *p*-terphenyl. Under irradiation, the spectral distribution of the emitted light is characteristic of the solute, *p*-terphenyl, and the intensity of the emission is increased over that expected by simply adding the intensities from the separate components. This is attributed to a transfer of excitation energy from the cyclohexane through the

benzene to the *p*-terphenyl. The degree of this transfer does not, however, appear to be sufficient to account for all the observed "protection" imparted to the solvent by the "protecting" solutes.

Although much work needs to be done in order to bring many of the reported yield values into agreement, the generally large disappearance values of aromatic scavengers such as anthracene, biphenyl, and benzene are much more consistent with mechanisms involving radical reactions than they are with mechanisms involving energy transfer. In the free-radical scavenging process, there should be the formation of certain kinds of combination products, the yield of which should increase with increased scavenger efficiency; and the types of products should be characteristic of the type of radical being scavenged as well as of the particular scavenger used.

EXPERIMENTAL

A. MATERIALS

Phillips' spectro-grade cyclohexane was used for irradiation. This lot was 99.98% pure and was used without further purification. Purity was determined by gas chromatography. Phillips' research-grade benzene, 99.93% pure, was used. Eastman white-label biphenyl and diphenyl ether were used as additives, as was Fisher Scientific zone refined naphthalene. Eastman white-label diphenylpicrylhydrazyl (DPPH) was recrystallized two times from carbon disulfide before using.

B. SAMPLE PREPARATION

Deaerated samples were prepared for irradiation by thoroughly outgassing a 10 × 150 mm. pyrex vial attached to a vacuum line. After outgassing, the vial was immersed in a Dry Ice- acetone bath and the continuous pumping on the vial stopped. A 2 ml. sample of the desired solution was placed in the vial by syringe through an appropriately placed rubber septum. After freezing, the free space above the sample was evacuated and then the continuous pumping stopped. The sample was allowed to melt and then was refrozen and reevacuated. This process was repeated at least four times before sealing the frozen sample while pumping.

Samples of cyclohexane containing various additives were prepared by weighing and the composition checked by gas chromatography.

The diphenylpicrylhydrazyl solutions were prepared by weighing the desired amount of DPPH into an appropriate volumetric flask and filling with boiled, hot cyclohexane. The samples were used without further deaeration.

C. RADIATION

The Denver Research Institute Co⁶⁰ source is very similar in design to one used at the University of Notre Dame¹¹ and is described in detail by Schmidt et al.⁴⁶. The source contains

approximately 1600 curies of Co^{60} . In the area of maximum intensity, the radiation dose rate was about 4.5×10^5 r/hr. All irradiation dose calculations were corrected for the Co^{60} decay or were determined from direct calibration.

A source calibration was made at different times during the research period using ceric sulfate reduction methods ($G = 2.39$) as the calibrating dosimeter⁵¹. The ceric sulfate for the calibrations was contained in sealed pyrex cells of the same type as used for sample irradiations, and the concentration was determined spectrophotometrically by measuring the absorbance at 3150 Å.

Just previous to the research period, the DRI source was cross-calibrated with a mobile 2500 curie Co^{60} source operated by Convair under Contract AF 33(616)-7547. The ratio of the intensity of the two sources as measured by the ceric sulfate dosimeter (DRI methods) and the ionization chamber methods used by Convair were within 0.3% of absolute agreement.

After the liquid samples were prepared for irradiation, they were lowered to the calibrated position in the source and left for a measured time period. After removal from the source, the samples were analyzed as quickly as possible. If any delay in analysis was anticipated, the samples were frozen until the analysis could be made.

Samples to be irradiated in the solid state were frozen to a crystalline state, placed in a Dewar flask containing Dry Ice and acetone, then placed in the source. Appropriate calibrations were made for these irradiations.

Irradiations involving the DPPH solutions required a much lower dose rate than that normally used. These irradiations were made at a position in the source which had a dose rate of 102 r/min., which was determined from calibration with self-reading ionization dosimeters.

D. PRODUCT ANALYSIS

a. Gas Chromatography (GC)

A Beckman GC-2 gas chromatograph with the Beckman Thermotrac column temperature programmer was used to determine the product yields from the irradiations. After considerable experimentation, it was found that the following instrument conditions would give the best results in the shortest period of time, and most of the data reported in subsequent sections were obtained from analyses under these conditions:

1. The thermal conductivity detector was maintained isothermally at 160°C. at a cell current of 300 milliamperes.
2. Helium carrier gas flow rate of 85 ml. per minute was maintained by a pressure of 40 p. s. i. to the instrument. This results in the column head pressure's being about 5 p. s. i. greater than the column exhaust pressure, which was always at prevailing atmospheric pressure.
3. Two matched, 12-foot, $\frac{1}{4}$ -inch O. D. aluminum columns packed with 60-80 mesh Chromosorb P (acid washed) on which was absorbed 20% (by weight) Carbowax 20M were used in the instrument. One column served as a reference column and the other as the analytical column.
4. The columns were operated isothermally at 60°C. for five minutes after sample injection; then the temperature was programmed nonlinearly to 215°C. during a fifteen minute period, after which isothermal operation at 215°C. was continued for the duration of the analysis.
5. Samples were introduced to the instrument by syringe. The sample size ranged from 0.005 to 0.02 ml., and was usually 0.01 ml.

Using the above conditions, the following compounds of interest in this research could be separated and resolved adequately for quantitative determinations: cyclohexane, cyclohexene, benzene, cyclohexylhexene, bicyclohexyl, a bicyclohexyldiene, phenylcyclohexane, biphenyl, naphthalene, and diphenyl ether. There are three radiolytically formed products which are eluted

from the column before cyclohexane which are not sufficiently resolved from each other to give a good quantitative analysis. These products, based on retention times in the column, appear to be n-hexane and two isomeric hexenes.

The quantitative determination of a particular yield component from the GC analysis was made by determining the instrument response to a known amount of the component. Component peak areas were measured with a Disc (Model KI) Integrator attached to the recorder, and the calibration factor was calculated in terms of numbers of molecules per square inch of instrument recorder response. This factor could then be used directly to determine the total number of component molecules formed by the irradiation; and division by the absorbed dose, in 100 ev. units, would give directly, the G value.

To determine the disappearance of an additive, the area response of the additive in the nonirradiated sample was made by several consecutive analyses. This was followed by several analyses of the irradiated sample containing the additive. The difference in area of the additive peak was calculated in terms of fraction of additive lost; and by knowing the original additive concentration, the number of additive molecules lost by the irradiation could be calculated.

In the tables of data are a few values related to the disappearance of cyclohexane which were determined by the procedure outlined in the previous paragraph. The accuracy of these values is considered quite low since the analysis involved measuring very small changes in the area of the component present in major quantities.

Since the Carbowax 20M. columns could not be used effectively above about 220°C., products boiling higher than any of those mentioned above were detected by using six-foot columns packed either with Apiezon L or SE-30 silicone gum. With these columns, the temperature could be programmed to 300°C. and high boiling additives and/or yield products detected.

b. Polymer Formation

A quantity of the irradiated sample was weighed into a tared 1-dram pyrex vial, and the low-boiling solvent and yield products were allowed to evaporate with low heat. After most of the low-boiling materials were removed, the vials were placed in a heated vacuum desiccator. The temperature was slowly raised to about 80°C., and the pressure was reduced to about 10 mm. Hg. The samples were allowed to remain under these conditions until a constant weight was reached, usually 36-48 hours. These conditions were sufficient to cause the complete evaporation of a two-gram sample of bicyclohexyl, which was used as a criterion for estimating when all the dimer products had been removed from the irradiated samples. After a constant weight had been reached, the weight of polymeric residue was determined. From this weight, the total weight of polymer produced could be calculated; and this weight divided by the molecular weight of cyclohexane times the radiation dose, in 100 ev. units, gives the G (polymer) value in terms of molecules of cyclohexane converted to polymer per 100 ev. of energy absorbed. After determining the final weight of the polymer, it was redissolved in a small quantity of cyclohexane and the sample analyzed by gas chromatography for the presence of additive and/or dimer products. The sample was then further analyzed by gas chromatography for the presence of higher boiling products.

c. Molecular Weight Determination

The molecular weight of the polymer residue was determined in a microebulliometer constructed after the design of Dimbat and Stross²². The instrument will permit the determination of a molecular weight on as little as 10 mg. of sample and can be used to determine molecular weights up to about 20,000. When a sample is a mixture of compounds, as the polymer products undoubtedly are, the indicated molecular weight is an average molecular weight. This value is biased toward the components of lower molecular weight. The molecular weight calculations were by methods recommended by Bonnar, Dimbat and Stross⁷.

d. Polymer Spectroscopy

The infrared spectrum of various polymer residues was obtained by depositing a polymer film onto a salt plate. The spectrum of the film was then recorded using a Beckman IR-7 Spectrophotometer.

Based on the interpretations of the infrared spectrum of the polymer derived from cyclohexane containing small amounts of aromatic solutes, evidently a considerable amount of the solute had become a part of the polymer. The following describes the procedure by which the amount of solute in the polymer was ascertained.

It is known that for any group of substituted aromatic compounds, i. e., alkyl benzenes, there are absorption bands in the ultraviolet region of the spectrum that are very characteristic of the aromatic moiety of the compound. Various substitutions on the aromatic structure shift these absorption bands very little, if at all, and have usually an insignificant effect on the intensity of the bands, so that the measurement of the intensity of a particular band can be related to the concentration of the aromatic structure present even though this structure is substituted in various ways.

In order to check the above, and as an example of the techniques developed, a cyclohexane solution containing very small but known quantities of biphenyl, amylbiphenyl, a diamylbiphenyl, 3-methylbiphenyl, 4-heptylbiphenyl, and 3-hexoxybiphenyl was prepared. An absorbance-concentration calibration curve from this mixture was prepared using the absorption at 250 m μ as a measure of the concentration of the biphenyl moiety. Several other solutions containing known amounts of biphenyl compounds were prepared and the concentration of "biphenyl moiety" determined from the absorbance and the calibration curve. In most cases, the determined value checked within less than 10% of the known value.

The above procedure was used to determine the amount of aromatic additive in the polymer derived from irradiations where benzene, biphenyl, naphthalene, and diphenyl ether were the solutes. Solute concentration was measured at 261.7 m μ .

for benzene, 250.0 mμ for biphenyl, 271.7 mμ for naphthalene, and 271.4 mμ for diphenyl ether using a Beckman DK-2 Spectrophotometer.

e. Free-Radical Determination

In order to determine quantitatively the number of free radicals formed by radiation, the radicals must be consumed by some reaction which competes favorably with their recombination; at the same time, the means by which these radicals are consumed must not interfere with the processes which form the radicals. The addition of a stable free radical A can react with radiation-formed radicals R through the reaction



If the disappearance of A can be conveniently followed, then it can be used as a measure of the disappearance of R; and if the reaction is efficient, the disappearance of R should be nearly equal to the formation of R. 1,1-Diphenylpicrylhydrazyl (DPPH) is a stable free radical and is highly colored in very dilute solutions. It reacts with other free radicals to form products which are colorless or at least with colors considerably different from the original DPPH color. This makes the concentration of DPPH solutions very easy to determine by colorimetric methods. If the radiation dose rate is sufficiently low and the DPPH concentration reasonably high, then the disappearance of DPPH should give a reasonable measure of the number of free radicals formed by radiation.

The solubility of DPPH in cyclohexane is quite low, being in the order of 5×10^{-5} M. at near saturation. Near-saturated solutions of DPPH in cyclohexane were prepared and certain experiments made in order to ascertain which parameters needed to be closely controlled in order to obtain reproducible results. These parameters are:

1. Elimination of excessive exposure to light is desirable.
2. Elimination of all water is necessary.
3. Low dose rate is required.

4. Deaeration by freezing and thawing under vacuum causes erratic results. Deaeration by bubbling cyclohexane-saturated nitrogen through the samples gives reproducible results.

5. All absorbence measurements must be made at a constant sample temperature.

When the above precautions are observed, the basic procedure for determining the free-radical yield is to determine the DPPH concentration before the sample is irradiated. This is done by measuring the absorbence at 511 m μ and determining the concentration from a concentration-absorbence calibration curve. The same procedure is followed after the sample has been irradiated. Converting the change in DPPH concentration to number of DPPH molecules disappearing and dividing by the absorbed dose in 100 ev. units gives G-(DPPH) or G (Radical).

RESULTS

A. PURE CYCLOHEXANE (LIQUID STATE IRRADIATIONS)

The yields of the products derived from the irradiation of pure cyclohexane are shown in Table V. These data show that the G value decreases with increasing radiation dose. This is shown graphically for cyclohexene and bicyclohexyl in Figures 2 and 3 respectively. The extrapolated to zero dose (initial yield, G_i) for cyclohexene is 2.4, and for bicyclohexyl the value is 2.0. The open chain C_6 hydrocarbons have a G_i value of 0.34. The values for cyclohexylhexene are quite varied; the G_i for this product is assumed to be 0.3. At a rather high dose, the polymer has a number average molecular weight of 464 and $G(\text{polymer}) = 1.91$. The polymer yield appears to decrease with decreasing dose (see Table XIV). Not enough data are available to estimate a $G_i(\text{polymer})$ value. High-temperature gas chromatography of the polymer showed the presence of a small amount of two compounds with retention times about equal to the retention times of o- and m-tercyclohexyl. It was estimated that the G value of these compounds was 0.05 and 0.09 respectively.

The infrared spectrum of the polymer, aside from showing the presence of cyclohexyl groups, indicates a rather large amount of unsaturation, which appears to be primarily trans olefins and vinyl groups. Aliphatic methylene chains are present. The general broad nature of the spectrum indicates a high degree of molecular complexity.

Although the data related to the disappearance of cyclohexane ($G-(\text{cyclohexane})$) are not considered to be accurate, they indicate that $G_i-(\text{cyclohexane})$ could be expected to be 5-6 and that there is a decrease in this value with increasing dose.

B. PURE CYCLOHEXANE (SOLID-STATE IRRADIATIONS)

A comparison of the yield of products derived from the irradiation of cyclohexane in the liquid and solid states can be made by examining some of the data in Tables XIV and XV. Irradiation

TABLE V
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF
CYCLOHEXANE

	Dose, 100 ev. $\times 10^{-20}$			
	0.44	1.0	1.66	0.046
G-(cyclohexane)	5.4	--	3.4	--
G(precyclohexane) ^a	0.30	0.27	0.24	--
G(cyclohexene)	1.36	0.90	0.56	1.82
G(cyclohexylhexene)	0.20	0.36	0.30	--
G(bicyclohexyl)	1.41	0.83	0.61	--
% (Wt.) Polymer	--	--	2.83	--
Polymer wt. , g/2 ml.	--	--	0.04401	--
Polymer molecular wt.	--	--	464	--
G(polymer)	--	--	1.91	--
^a Sum of three components emerging from GC column before cyclohexane. Probably open chain C ₆ hydrocarbons.				

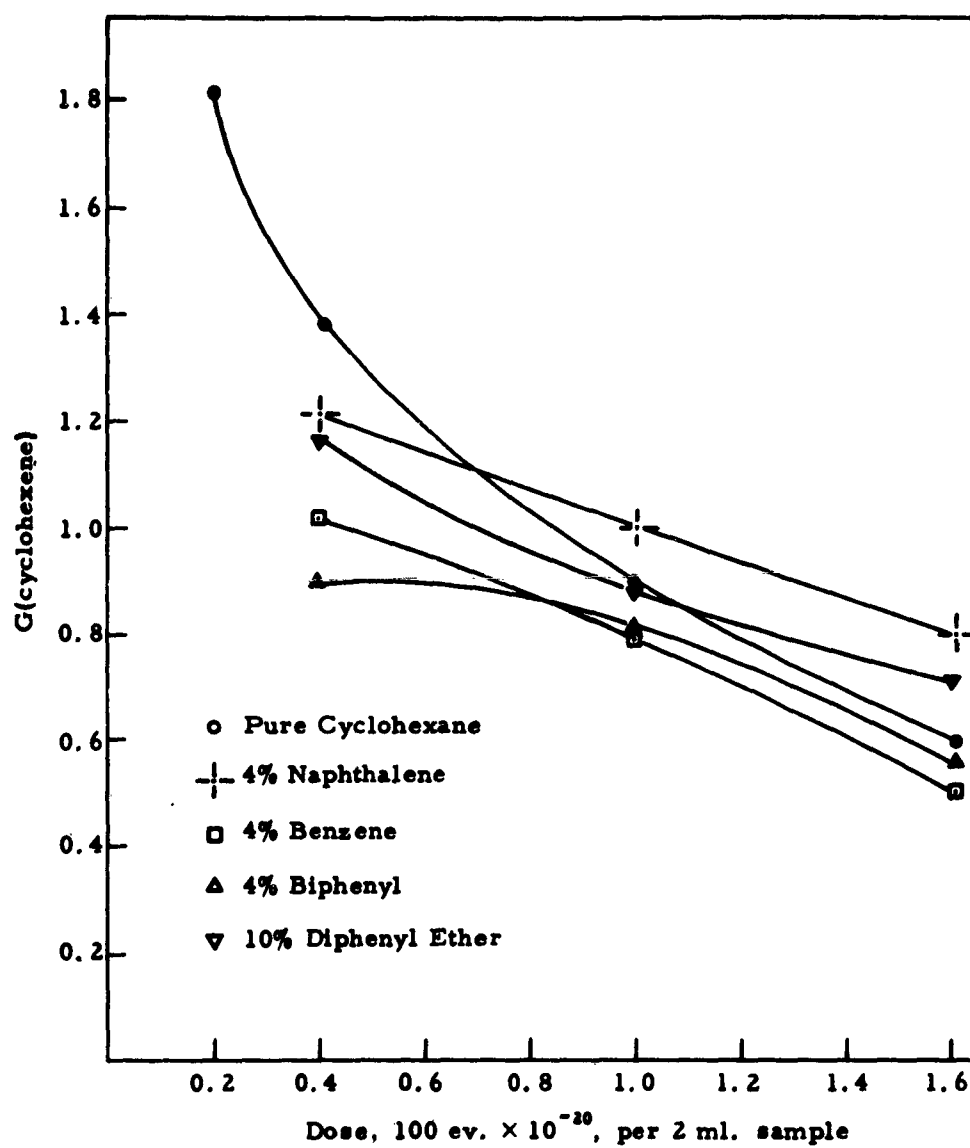


Figure 2. Cyclohexene Yield from Cyclohexane Solutions as a Function of Dose.

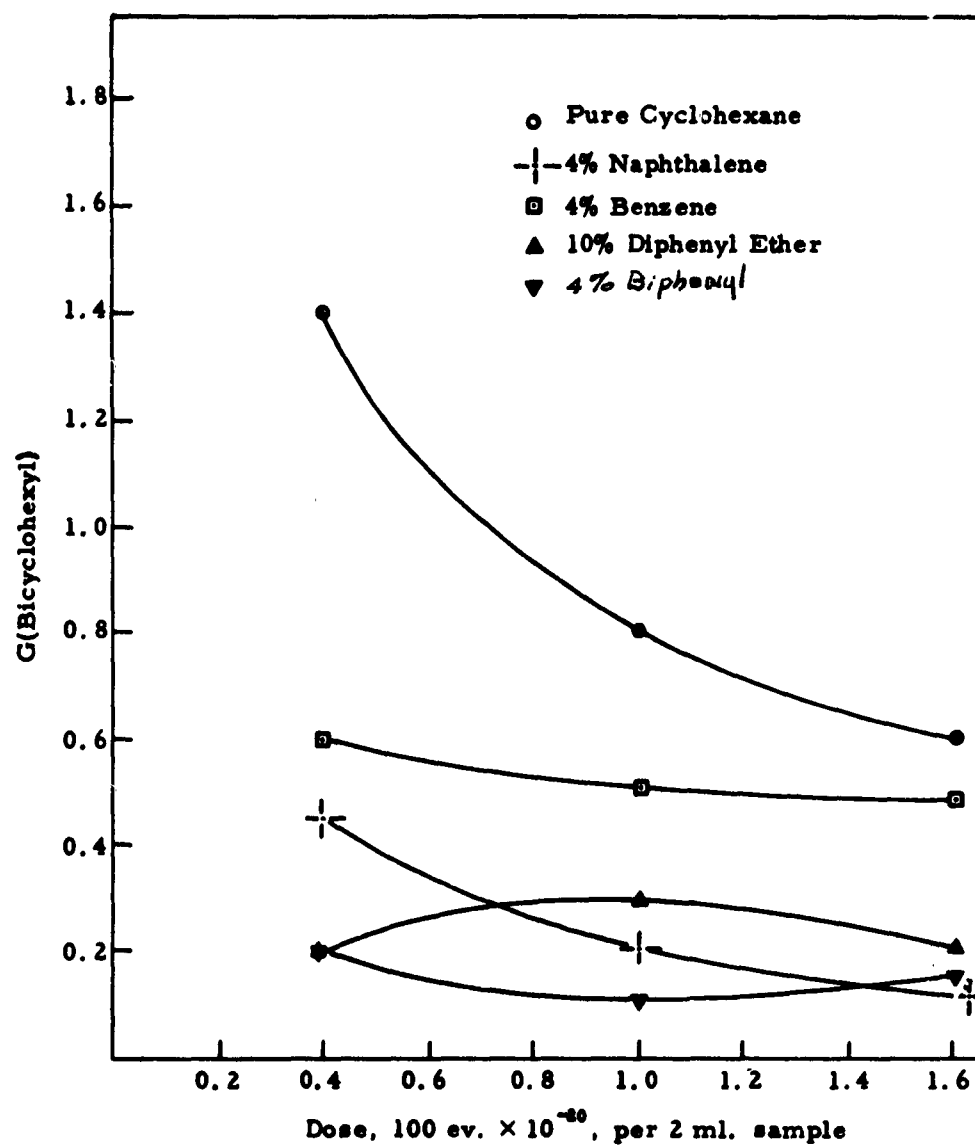


Figure 3. Bicyclohexyl Yield from Cyclohexane Solutions as a Function of Dose.

in the solid state significantly reduces the yield of C_6 hydrocarbons, cyclohexene, and bicyclohexyldiene. Cyclohexylhexene and bicyclohexyl are increased. The yield of polymer in a solid-state irradiation is reduced by about 25%.

C. CYCLOHEXANE-BENZENE SOLUTIONS (LIQUID-STATE IRRADIATIONS)

The types of compounds formed in the radiolysis of these solutions are the same as in the radiolysis of cyclohexane with the exception of the formation of phenylcyclohexane. The latter compound was definitely identified by its behavior on Apiezon L and Carbowax 20 M GC columns and by collecting the compound from the GC separation and obtaining the infrared spectrum of the compound, which was found to be identical with that of phenylcyclohexane.

The data in Tables VI, VII, VIII and XIV show the yield values of the various products over a wide range of benzene concentrations and at varying and constant doses. The relation of cyclohexene yield to dose (at constant benzene concentration) is shown in Figure 2. The $G_i(\text{cyclohexene})$ is 1.3. From Figure 3, the $G_i(\text{bicyclohexyl})$ from cyclohexane containing 4% benzene is 0.7. Figure 4 shows the relation of cyclohexene and bicyclohexyldiene yields to the benzene concentration at a constant dose. The effect of benzene concentration on the yield of bicyclohexyl (at constant dose) is shown in Figure 5. The disappearance of benzene as a function of dose is shown in Figure 6. Figure 7 shows the effects of benzene concentration on the yields of cyclohexene bicyclohexyl, bicyclohexyldiene, and phenylcyclohexane. The yield of phenylcyclohexane is plotted as a function of total energy absorbed by the sample and also as a function of energy absorbed by the sample and as a function of energy absorbed only by the benzene in Figure 8.

The molecular weight of the polymer is 430 (Table VI). The variation in polymer yield as a function of benzene concentration is shown in Table XIV. Examination of the infrared spectrum of the polymer reveals cyclohexyl groups and considerable aromatic compositions. Most of the aromatic portion of the

TABLE VI
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF
CYCLOHEXANE CONTAINING ABOUT 4% BENZENE

	0.44	Dose, 100 ev. $\times 10^{-20}$	
		1.0	1.66
G-(cyclohexane)	--	--	2.9
G(benzene) ^a	11.3	14.7	11.8
G(precyclohexane) ^b	0.29	0.24	0.19
G(cyclohexylhexane)	0.17	0.23	0.20
G(bicyclohexyl)	0.60	0.51	0.46
G(phenylcyclohexane)	0.24	0.25	0.18
% benzene lost	4.2	12.9	17.1
G-(benzene) ^c	0.46	0.62	0.50
% (wt.) polymer	--	--	2.8
Polymer wt. , g. /2 ml.	--	--	0.04383
Polymer molecular wt.	--	--	430
G(polymer) ^d	--	--	2.0

^a Calculated on basis of electron fraction benzene, $E_a = 0.0420$.

^b Sum of three components emerging from GC column before cyclohexane. Probably open chain C_6 hydrocarbons. ^c Calculated on basis of total energy absorbed by sample. ^d In terms of cyclohexane converted to polymer.

TABLE VII
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF
CYCLOHEXANE CONTAINING VARYING AMOUNTS
OF BENZENE

	Electron Fraction Benzene (Ea) ^a				
	0	0.00131	0.0026	0.042	0.441
G(precyclohexane) ^b	0.38	0.24	0.24	0.31	0
G(cyclohexene)	1.84	1.50	1.42	1.06	0.34
G(cyclohexylhexane)	0.11	0.09	0.07	0.07	0.07
G(bicyclohexyl)	1.38	0.95	0.89	0.51	0.04
G(bicyclohexyldiene)	0.44	0.18	0.22	0.07	0
G(phenylcyclohexane)	--	.04	.04	.23	.24
G-(benzene) ^c	--	90.7	70.1	18.2	--
G-(benzene) ^d	--	0.11	0.12	0.77	--

^a Dose = 0.24×10^{20} 100 ev. ^b Sum of three components emerging from GC column before cyclohexane. ^c Calculated on basis of electron fraction benzene. ^d Calculated on basis of total energy absorbed by sample.

TABLE VIII
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF CYCLOHEXANE CONTAINING
VARYING AMOUNTS OF BENZENE

	0	0.8043	0.6023	0.4011	0.2135	0.1113	0.0458	0.0217	0.0085	0.00173	.00080
G(percyclohexane) ^b	0.25	0.12	--	--	--	0.15	0.25	0.25	0.19	0.37	0.25
G(cyclohexene)	1.84	0.12	0.24	0.36	0.48	0.60	1.02	0.94	1.26	1.38	1.44
G(cyclohexylhexene)	0.25	trace	--	0.03	--	0.05	0.06	0.09	0.10	0.12	0.22
G(bicyclohexyl)	1.36	0.03	--	0.03	0.15	0.20	0.49	0.53	0.81	0.87	0.90
G(bicyclohexyldiene) ^c	0.31	trace	--	trace	0.03	0.03	0.09	0.09	0.19	0.21	0.22
G(phenylcyclohexane) ^c	--	0.09	0.11	0.15	0.22	0.28	0.31	0.20	0.14	0.06	trace
G-(benzene) ^d	--	3.6	--	--	6.8	--	25.5	33.5	34.0	41.5	40.4
G(phenylcyclohexane) ^d	--	0.11	0.18	.37	1.03	2.51	6.77	9.22	16.46	34.7	--
G-(benzene) ^e	--	18.5	--	--	18.3	--	12.1	7.37	2.89	0.71	0.32

^a Dose = 0.26×10^{16} 100 ev. per 2 ml. sample. ^b Sum of three components emerging from GC column before cyclohexane.

^c Calculated on basis of total energy absorbed by sample. ^d Calculated on basis of electron fraction benzene. ^e Calculated on

basis of energy absorbed by cyclohexane, Ec.

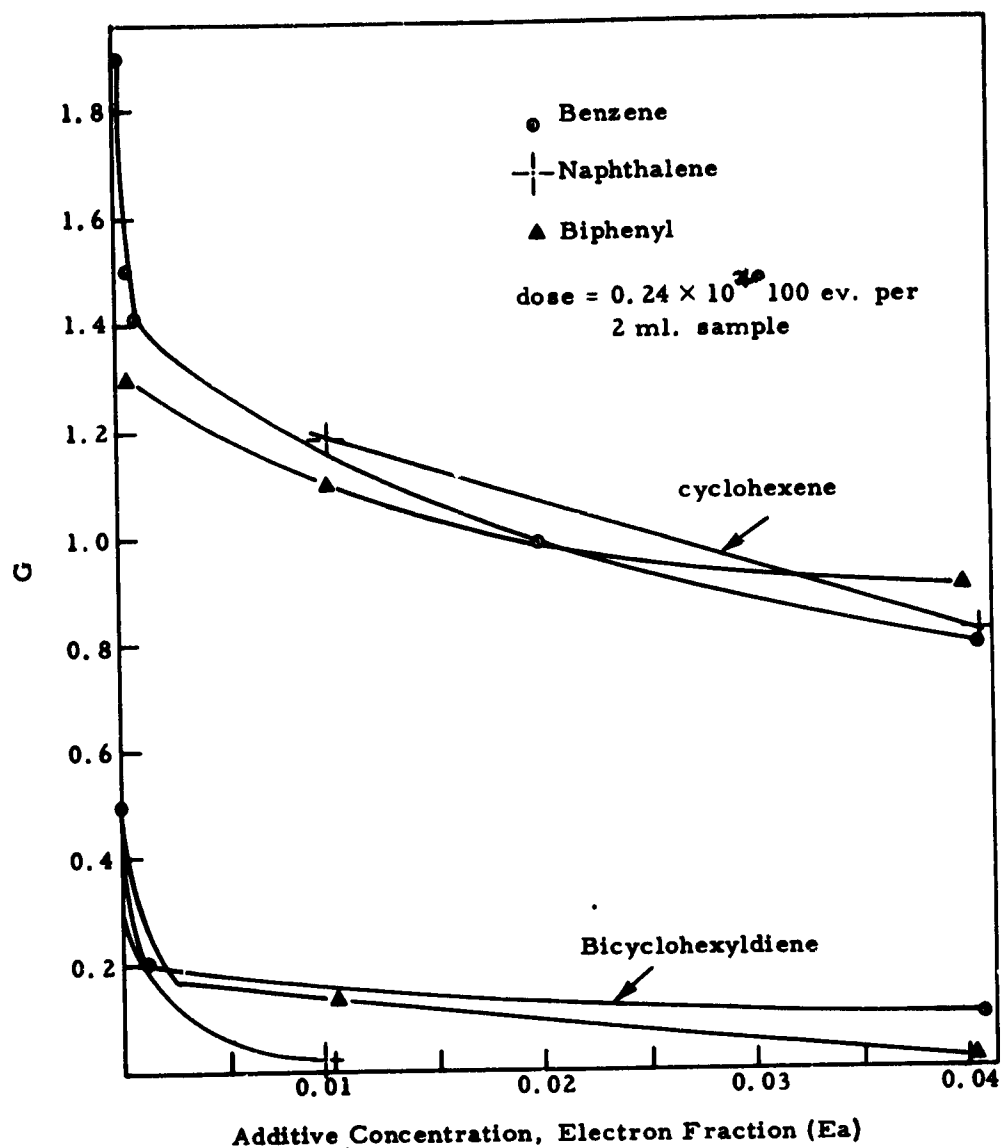


Figure 4. Yield of Cyclohexene and Bicyclohexyldiene as a Function of Additive Concentration.

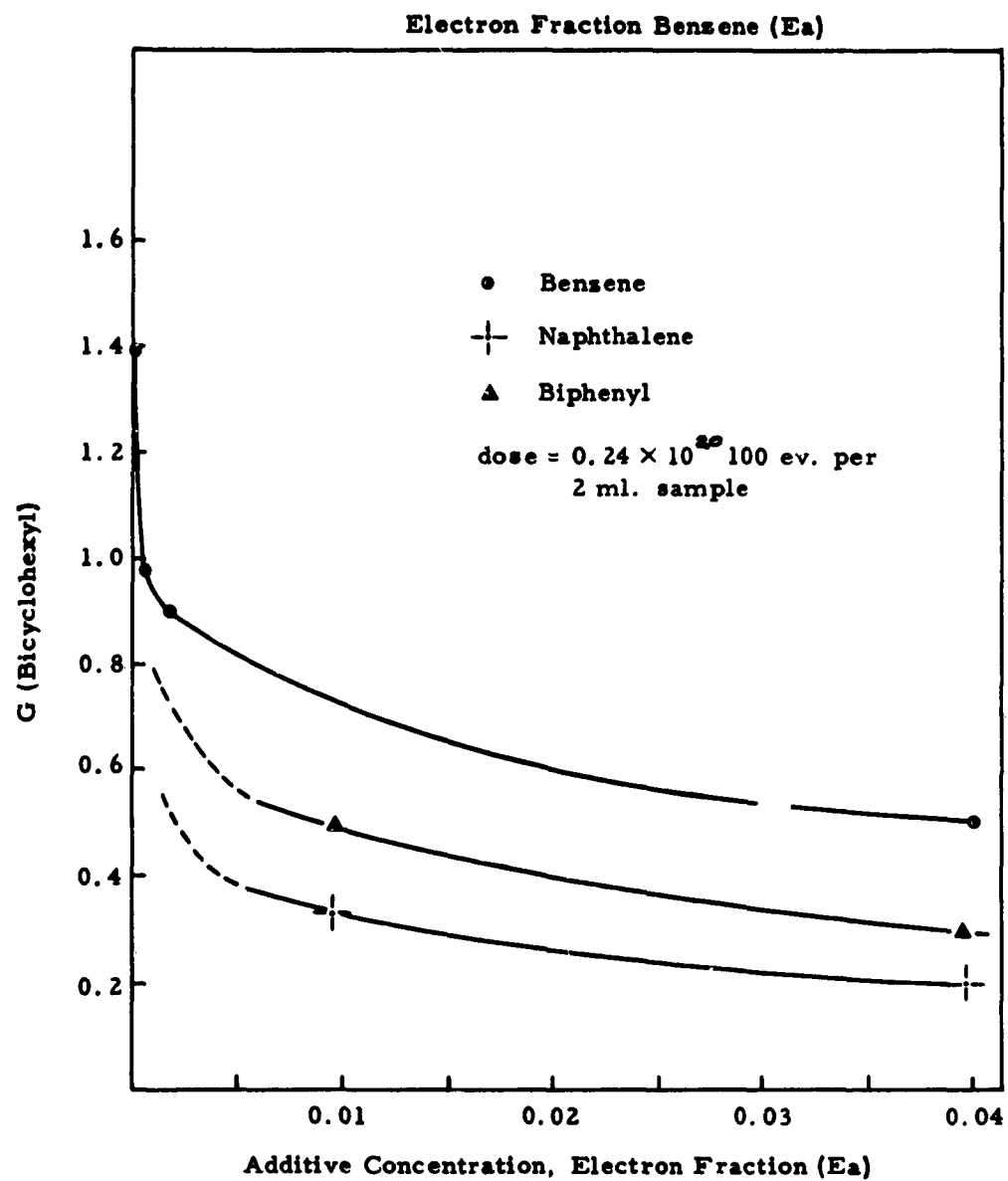


Figure 5. Yield of Bicyclohexyl as a Function of Additive Concentration.

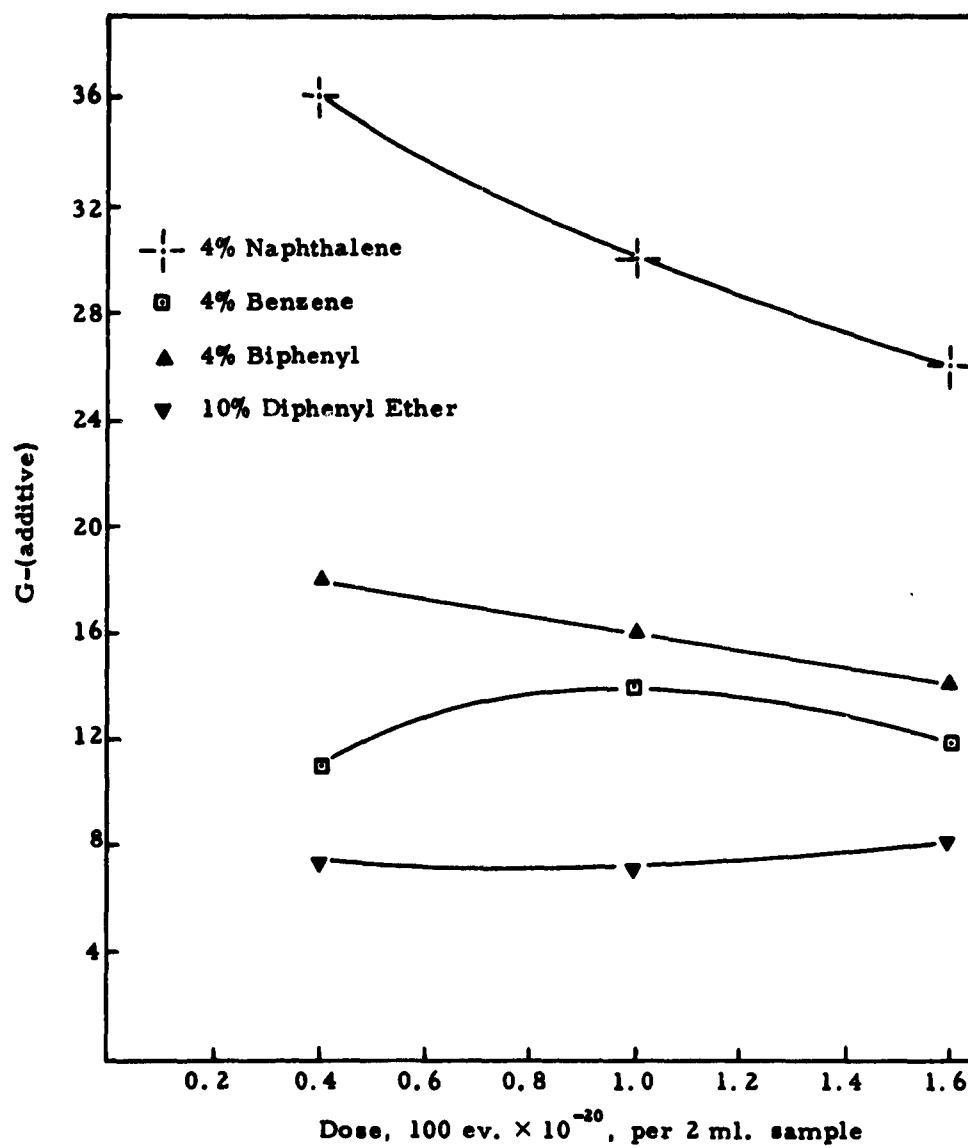


Figure 6. Disappearance of Additive in Cyclohexane Solutions as a Function of Dose.

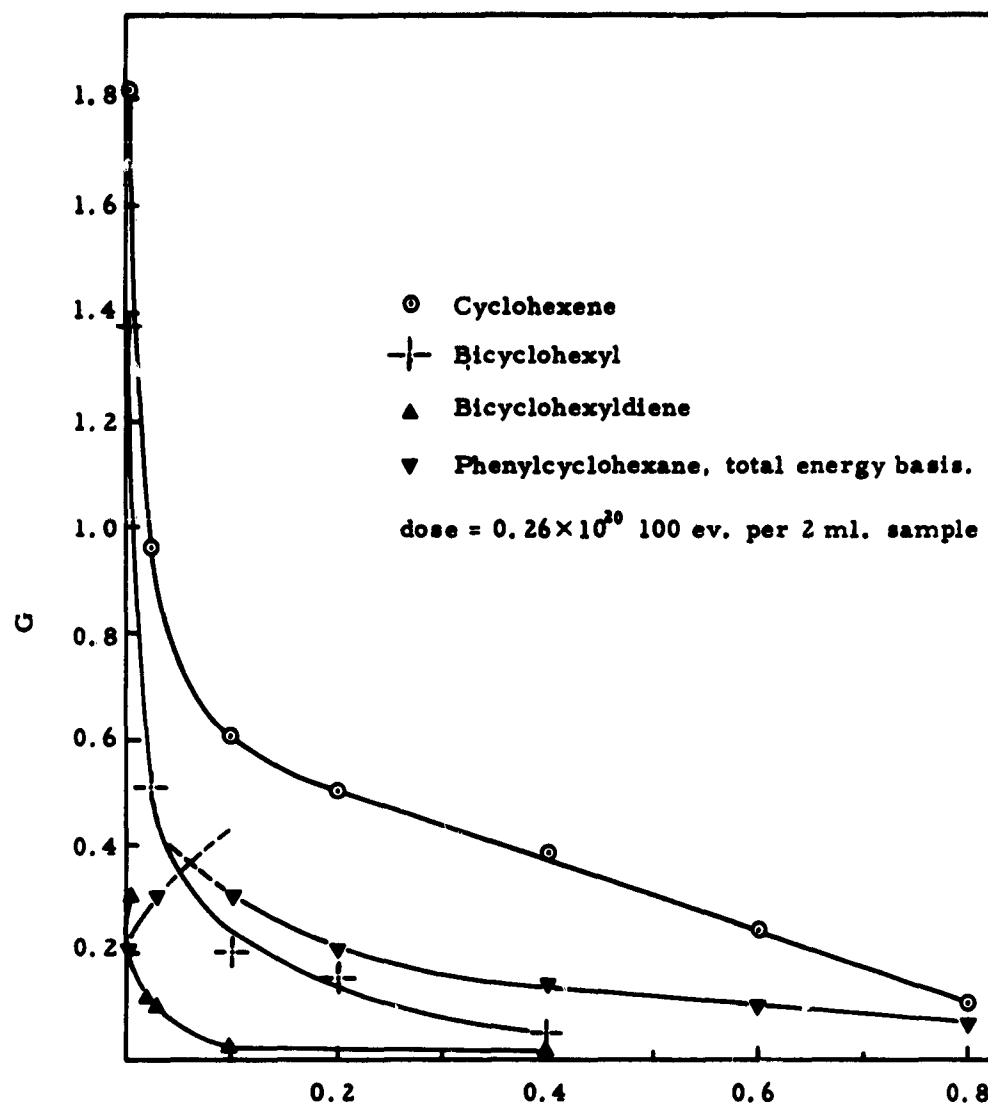


Figure 7. Product Yield as a Function of Benzene Concentration.

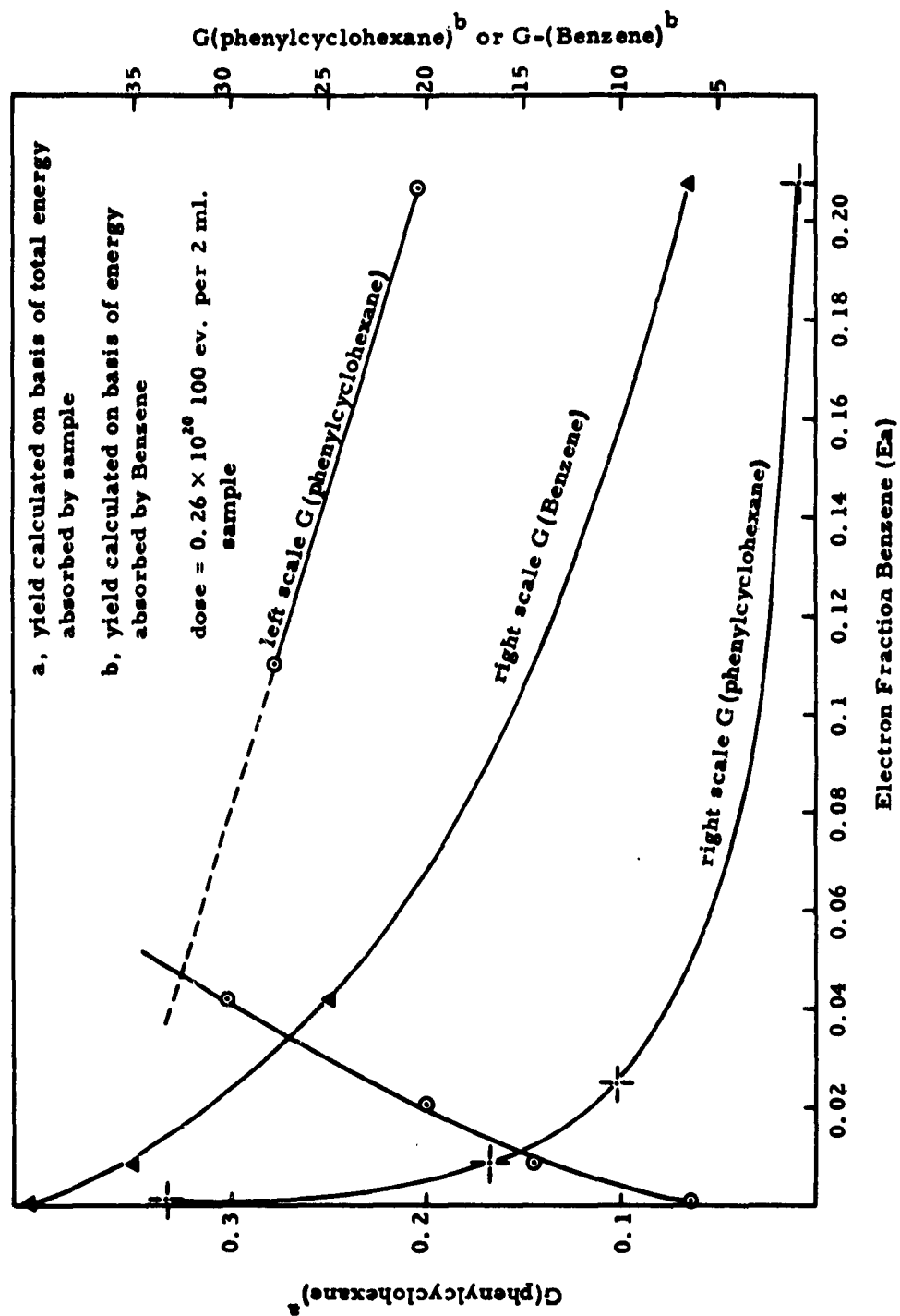


Figure 8. Phenylcyclohexane Yield and Benzene Disappearance as a Function of Benzene Concentration.

polymer appears to be mono-substituted phenyl groups. There are also some para-substituted phenyl groups but little evidence for ortho- or meta-substitution. Trans-olefin configurations are present in rather large amounts and appear to be in conjugation with aryl structures. The presence of more than four consecutive adjacent methylene groups is observed, which is indicative of cyclohexyl ring cleavage.

The ultraviolet determination of the aromatic composition of the polymer reveals that $34.7 \pm 2.8\%$ (Wt.) of the polymer is composed of phenyl groups.

Gas chromatographic analysis of the polymer showed the presence of three detectable components. Two of these were identical to those found in the cyclohexane polymer and are o- and m-tercyclohexyl ($G = 0.03$ and 0.06 respectively). The third component, based on retention time, corresponds to p-dicyclohexylbenzene, $G = 0.12$.

D. CYCLOHEXANE-BENZENE SOLUTIONS (SOLID-STATE IRRADIATIONS)

Table XIV shows the data resulting from the irradiation of solutions of cyclohexane containing varying amounts of benzene. It should be noted that irradiation in the solid state results in several significant changes in product distribution.

E. CYCLOHEXANE-NAPHTHALENE SOLUTIONS (LIQUID-STATE IRRADIATIONS)

The data derived from the irradiation of cyclohexane solutions containing naphthalene are shown in Tables IX and X. Some of the pertinent data are shown graphically in Figures 2-6. These data will be discussed in later sections.

It should be noted (Table X) that the molecular weight of the polymer is significantly lower than that of other polymers; also, the yield of polymer is higher. The infrared spectrum of the polymer shows the presence of cyclohexyl groups and a large quantity of alpha-substituted naphthalene compounds. A lesser amount of beta-substituted naphthalene compounds is indicated. There is only a slight indication of trans-unsaturation in the polymer.

TABLE IX
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF
CYCLOHEXANE CONTAINING VARYING AMOUNTS OF
NAPHTHALENE

	Electron Fraction of Naphthalene (Ea) ^a		
	0	0.009	0.0379
G(precyclohexane) ^b	0.38	0.27	0.29
G(cyclohexene)	1.84	1.16	0.80
G(cyclohexylhexene)	0.11	0.02	trace
G(bicyclohexyl)	1.38	0.33	0.21
G(bicyclohexyldiene)	0.44	trace	0
G-(naphthalene) ^c	--	122	32.2
G-(naphthalene) ^d	--	1.1	1.2

^a Dose = 0.24×10^{20} 100 ev. ^b Sum of three components emerging from GC column before cyclohexane. Probably open chain C₆ hydrocarbons. ^c Calculated on basis of electron fraction naphthalene. ^d Calculated on basis of total energy absorbed by sample.

TABLE X
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF
CYCLOHEXANE CONTAINING ABOUT 4% NAPHTHALENE

	Dose, 100 ev. , $\times 10^{-20}$			
	.44	.52	1.0	1.66
G ₁ (cyclohexane)	5.1	--	3.3	5.1
G ₂ -(naphthalene) ^a	36.1	28.8	29.8	25.9
G <pre>cyclohexane</pre> ^b	0.32	0.41	0.29	0.23
G(cyclohexene)	1.24	1.34	1.00	0.80
G(cyclohexylhexene)	0.04	0.05	0.12	0.13
G(bicyclohexyl)	0.45	0.38	0.20	0.12
% naphthalene lost	20.0	19.3	38.7	55.4
G ₂ -(naphthalene) ^c	1.37	1.10	1.13	0.98
% (wt.) polymer	--	--	--	4.36
Polymer wt. , g./2ml.	--	--	--	0.06799
Polymer molecular wt.	--	--	--	382
G(polymer) ^d	--	--	--	3.1

^a Calculated on basis of electron fraction naphthalene, $E_a = 0.0378$. ^b Sum of three components emerging from GC column before cyclohexane. Probably open chain C₆ hydrocarbons.
^c Calculated on basis of total energy absorbed by sample.
^d In terms of cyclohexane converted to polymer.

High-temperature gas chromatographic analysis of the polymer showed two components emerging in the region of C_{18} hydrocarbons. Based on the retention time and the information derived from the infrared spectrum of the polymer, these components appear to be α -cyclohexylnaphthalene ($G = 0.40$) and β -cyclohexylnaphthalene ($G = 0.08$). Ultraviolet spectroscopy indicates that the polymer contains $44.6 \pm 3.1\%$ naphthyl derivatives.

F. CYCLOHEXANE-NAPHTHALENE SOLUTIONS (SOLID-STATE IRRADIATIONS)

The data for these irradiations are shown in Table XV.

G. CYCLOHEXANE-BIPHENYL SOLUTIONS (LIQUID-STATE IRRADIATIONS)

The irradiation data for these solutions are shown in Tables XI and XII and Figures 2-6.

The infrared spectrum of the polymer shows the presence of biphenyl groupings. The greater part of the substitutions on the biphenyl moiety appears to be in the para-position. There is only a small amount of trans-unsaturation in the polymer.

Ultraviolet determination of biphenyl composition in the polymer gives a value of $21.6 \pm 15.1\%$. The high error in this determination is the result of a broad absorption, apparently not associated with the biphenyl structure, appearing in the spectral region of measurement.

The GC analysis of the polymer showed the presence of o-tercyclohexyl ($G = 0.09$) and another compound tentatively identified as p-cyclohexylbiphenyl ($G = 0.12$).

TABLE XI
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF
CYCLOHEXANE CONTAINING VARYING AMOUNTS
OF BIPHENYL

	Electron Fraction Biphenyl (Ea) ^a			
	0	0.0014	0.0094	0.0379
G(precyclohexane) ^b	0.38	0.24	0.22	0.22
G(cyclohexene)	1.84	1.30	1.10	0.92
G(cyclohexylhexane)	0.11	0.08	0.04	0.03
G(bicyclohexyl)	1.38	0.93	0.47	0.27
G(bicyclohexyldiene)	0.44	--	0.11	trace
G-(biphenyl) ^c	--	71.1	51.2	23.1
G-(biphenyl) ^d	--	0.10	0.48	0.87

^a Dose = 0.24×10^{20} 100 ev. ^b Sum of three components emerging from GC column before cyclohexane. ^c Calculated on basis of electron fraction biphenyl. ^d Calculated on basis of total energy absorbed by sample.

TABLE XII
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF
CYCLOHEXANE CONTAINING ABOUT 4% BIPHENYL

	Dose, 100 ev., $\times 10^{-20}$		
	0.44	1.0	1.66
G-(cyclohexane)	5.7	2.8	1.4
G-(biphenyl) ^a	18.0	17.1	14.1
G(precyclohexane) ^b	0.29	0.25	0.20
G(cyclohexane)	0.88	0.80	0.58
G(cyclohexylhexane)	--	0.18	0.15
G(bicyclohexyl)	0.22	0.26	0.22
% biphenyl lost	12.2	26.7	36.2
G-(biphenyl) ^c	0.68	0.65	0.53
% (wt.) polymer	--	--	3.5
Polymer wt., g/2 ml.	--	--	0.05514
Polymer molecular wt.	--	--	440
G(polymer) ^d	--	--	2.5

^a Calculated on basis of electron fraction biphenyl, $E_a = 0.0379$.

^b Sum of three components emerging from GC column before cyclohexane. Probably open chain C_6 hydrocarbons. ^c Calculated on basis of total energy absorbed by sample. ^d In terms of cyclohexane converted to polymer.

H. CYCLOHEXANE-BIPHENYL SOLUTIONS (SOLID-STATE IRRADIATIONS)

The results of these analyses are shown in Table XVI.

I. CYCLOHEXANE-DIPHENYL ETHER SOLUTIONS (LIQUID-STATE IRRADIATIONS)

Table XIII and Figures 2, 3 and 6 show the results of these irradiations.

The infrared spectrum of the polymer shows the presence of cyclohexyl groups and an aromatic ether. Much of the aromatic portion of the polymer appears to be in the form of monosubstituted phenyl groups, which suggests a structure similar to phenoxycyclohexane rather than cyclohexyl-substituted diphenyl ether. From previous work with the radiolysis of diphenyl ether, it is known that the ether bond can be cleaved by the action of free radicals.⁶ The resulting products derived from the reaction with cyclohexyl radicals could very easily possess the structures that are indicated in the spectrum. The spectrum shows the presence of only a small amount of unsaturation.

The polymer has a diphenyl ether composition of $37.8 \pm 5.0\%$. Only one product was detected by gas chromatography, and this corresponds to o-tercyclohexyl ($G = 0.06$).

J. FREE-RADICAL STUDIES

The data in Tables XVII and XVIII were obtained from irradiating 3 ml. samples of cyclohexane containing different concentrations of DPPH. Some of these data are shown graphically in Figures 9 and 11. Table XIX contains the data derived from irradiating at constant dose, cyclohexane DPPH solutions containing varying amounts of benzene. These data are plotted in Figures 10 and 11. Figure 12 shows the effects of 1% benzene and 1% naphthalene on the yield of free radicals as determined by the disappearance of DPPH.

TABLE XIII
ANALYTICAL RESULTS FROM THE RADIOLYSIS OF
CYCLOHEXANE CONTAINING ABOUT 10% DIPHENYL ETHER

	Dose, 100 ev., $\times 10^{-20}$		
	0.44	1.0	1.66
G-(cyclohexane)	--	4.6	4.5
G-(diphenyl ether) ^a	7.1	6.8	7.6
G(precyclohexane) ^b	0.29	0.23	0.19
G(cyclohexene)	1.16	0.88	0.66
G(cyclohexylhexane)	--	0.16	--
G(bicyclohexyl)	0.22	0.15	0.15
G(benzene)	0.13	0.09	0.09
G(phenol)	0.13	0.13	0.11
G(phenylcyclohexane)	0.013	0.025	0.020
% diphenyl ether lost	5.3	11.7	21.4
G-(diphenyl ether) ^c	0.27	0.27	0.29
% (wt.) polymer	--	--	6.1
Polymer wt., g./2 ml.	--	--	0.09481
Polymer molecular wt.	--	--	415
G(polymer) ^d	--	--	4.5

^a Calculated on basis of electron fraction diphenyl ether, $E_a = 0.0939$. ^b Sum of three components emerging from GC column before cyclohexane. Probably open chain C_6 hydrocarbons.
^c Calculated on basis of total energy absorbed by sample.
^d In terms of cyclohexane converted to polymer.

TABLE XV
LIQUID- AND SOLID-STATE RADIOLYSIS OF CYCLOHEXANE-NAPHTHALENE SOLUTIONS

	0		E _a ^a			
			0.0090		0.0379	
	liquid	solid	liquid	solid	liquid	solid
G(precyclohexane) ^b	0.36	0.21	0.31	0.16	0.25	0.20
G(cyclohexene)	1.76	1.06	1.26	0.94	0.80	0.96
G(cyclohexylhexene)	0.13	0.26	0.05	0.16	0.03	0.16
G(bicyclohexyl)	1.29	1.46	0.34	1.43	0.20	1.24
G(bicyclohexyldiene)	0.38	trace	trace	0.03	0	0.07
G-(naphthalene) ^c	--	--	115	0	35	18.4

^a Dose = 0.25 × 10²⁰ 100 ev. per sample. ^b Sum of three components emerging from GC column before cyclohexane. Probably open chain C₆ hydrocarbons. ^c Calculated on basis of electron fraction naphthalene.

TABLE XVI
LIQUID- AND SOLID-STATE RADIOLYSIS OF CYCLOHEXANE-BIPHENYL SOLUTIONS

	0		0.00143		Ea ^a		0.00942		0.0379	
	liquid	solid	liquid	solid	liquid	solid	liquid	solid	liquid	solid
G(precyclohexane) ^b	0.36	0.21	0.25	0.20	0.21	0.10	0.21	0.10	0.21	0.10
G(cyclohexene)	1.76	1.06	1.40	1.04	1.08	0.98	0.98	0.98	0.98	0.88
G(cyclohexylhexene)	0.13	0.26	0.09	0.16	0.05	0.15	0.03	0.16		
G(bicyclohexyl)	1.29	1.46	0.93	1.46	0.48	1.36	0.25	1.30		
G(bicyclohexyldiene)	0.38	trace	0.20	0.03	0.10	0.03	trace	0.03		
G-(biphenyl) ^c	--	--	63	0	45	2.2	23	6.7		

a Dose = 0.25 X 10²⁰ 100 ev. per sample. b Sum of three components emerging from GC column before cyclohexane. Probably open chain C₆ hydrocarbons. c Calculated on basis of electron fraction biphenyl.

TABLE XVII
THE RATE OF FREE-RADICAL FORMATION IN IRRADIATED
CYCLOHEXANE SOLUTIONS

Irradiation Time, minutes ^a	Dose 100 ev. $\times 10^{-14}$	DPPH $\bar{M} \times 10^{-5}$	G-(DPPH) ^b
0	0	4.61	0
8	11.07	3.77	13.7
16	22.14	2.82	14.6
16 ^c	22.14	3.09	12.4
32	44.29	0.59	16.4

^a Air present during irradiation. ^b G-(DPPH) = G(radical).
^c Solution contained 1.2% benzene.

TABLE XVIII
DATA OBTAINED FROM THE IRRADIATION OF CYCLOHEXANE CONTAINING
 $5.112 \times 10^{-5} \text{M}$ and $2.56 \times 10^{-5} \text{M}$ DIPHENYLPICRYLHYDRAZYL (DPPH) AT VARYING
IRRADIATION DOSES

Irradiation Time, minutes ^a	Dose 100 ev. $\times 10^{-14}$	(DPPH) remain- ing, $\text{M} \times 10^{-5}$	(DPPH) $\text{M} \times 10^{-5}$	(DPPH), No. of molecules $\times 10^{-15}$	G-(DPPH)
0	0	5.112	0	--	--
2.5	3.6	4.83	.28	5.06	14.36
5.0	7.2	4.54	.57	10.30	14.31
10	14.4	3.92	1.19	21.50	14.93
20	28.8	2.48	2.63	47.52	16.50
30	43.2	1.07	4.04	73.00	16.90
40	57.6	0.25	4.86	87.82	15.25
0	0	2.56	0	--	--
2.5	3.6	2.22	.32	5.78	16.05
5	7.2	1.74	.82	14.82	20.58
10	14.4	1.00	1.56	28.19	19.58
15	21.6	0.45	2.11	38.13	17.65
20	28.8	0.10	2.46	44.45	15.43
^a Air present during irradiation.					

TABLE XIX
DATA OBTAINED FROM THE IRRADIATION OF CYCLOHEXANE CONTAINING
5.112 $\times 10^{-5}$ M DIPHENYLPICRYLHYDRAZYL AND VARYING CONCENTRATIONS OF
BENZENE AT A CONSTANT DOSE

Dose, 100 ev. $\times 10^{-14}$	^a Percent Benzene	(DPPH) remain- ing, $M \times 10^{-5}$	(DPPH) of molecules $M \times 10^{-5} \times 10^{-15}$	(DPPH), No. of molecules $\times 10^{-15}$	G-(DPPH) benzene	$\Delta G(\text{DPPH})$ due to benzene
28.8	0	2.48	2.63	47.52	16.50	0
28.8	0.1	2.67	2.44	44.09	15.31	1.19
28.8	0.5	2.92	2.19	39.57	13.74	2.76
28.8	1.003	3.05	2.06	37.22	12.92	3.58
28.8	2.99	3.18	1.93	34.87	12.11	4.39
^a Air present during irradiation.						

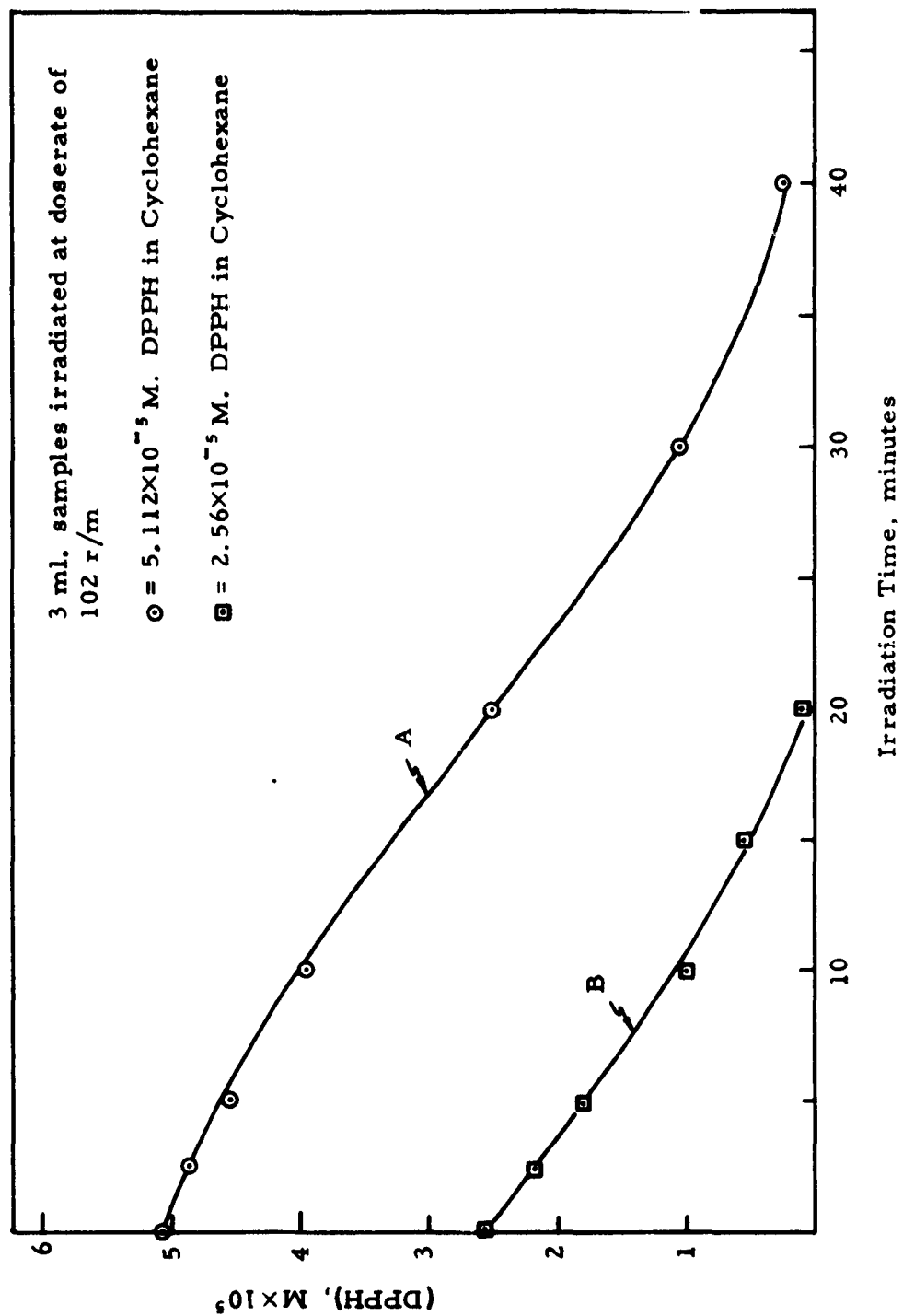


Figure 9. Change in DPPH Concentration with Varying Dose.

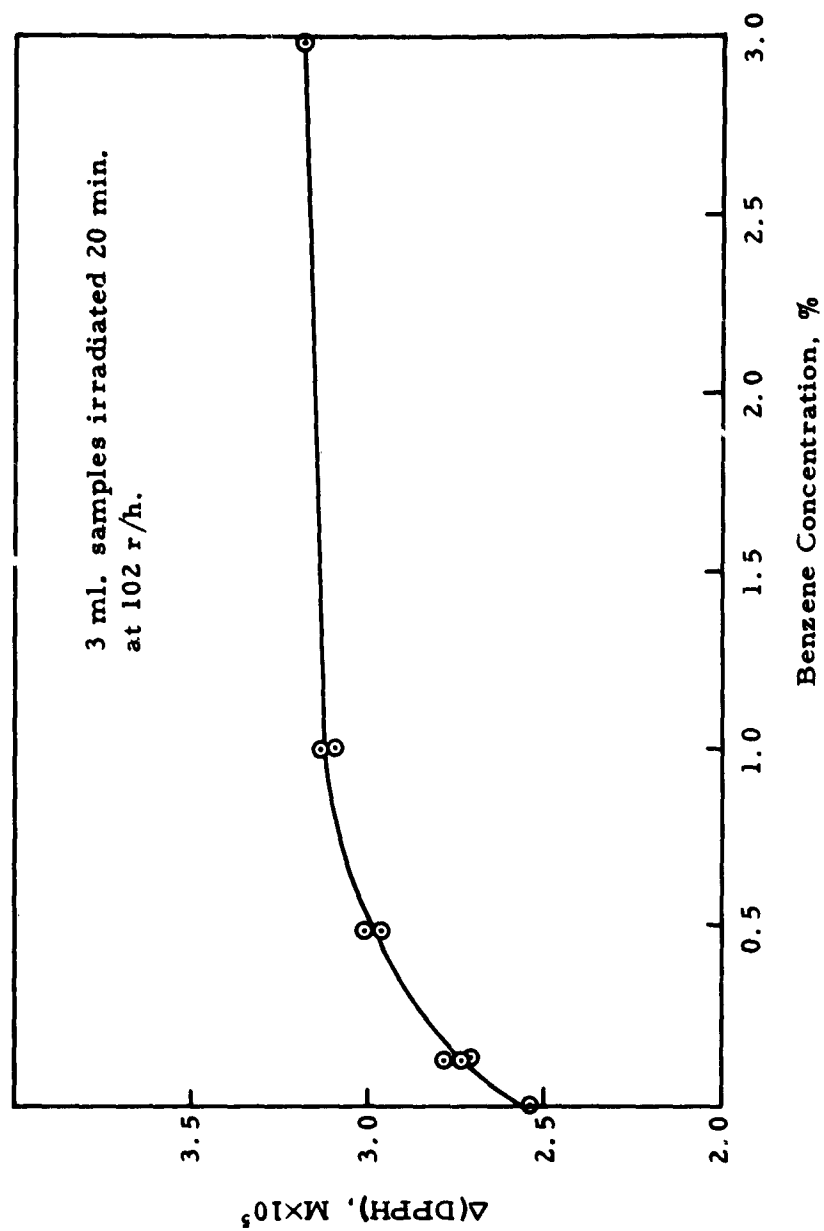


Figure 10. Change in DPPH Concentration in Cyclohexane Containing Varying Amounts of Benzene.

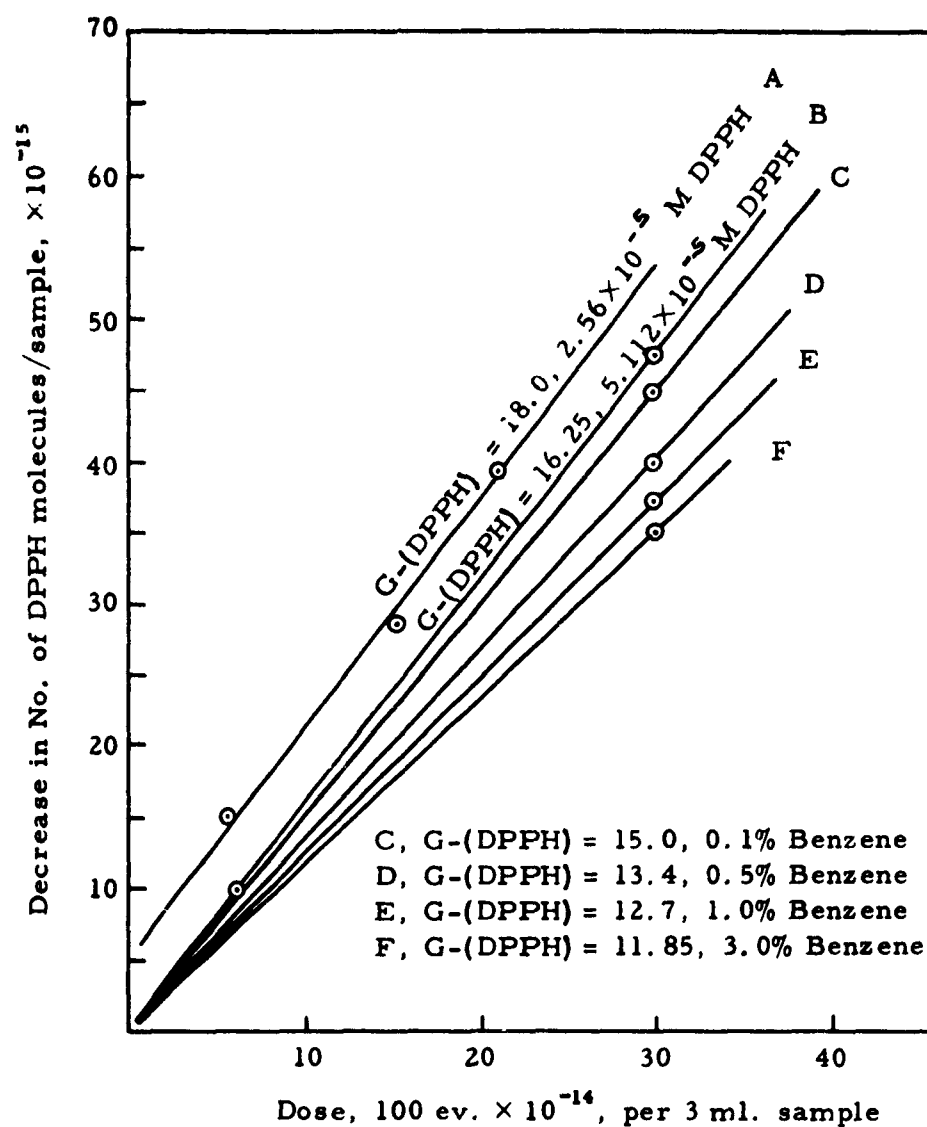


Figure 11. Change in G-(DPPH) Due to the Presence of Benzene in Cyclohexane.

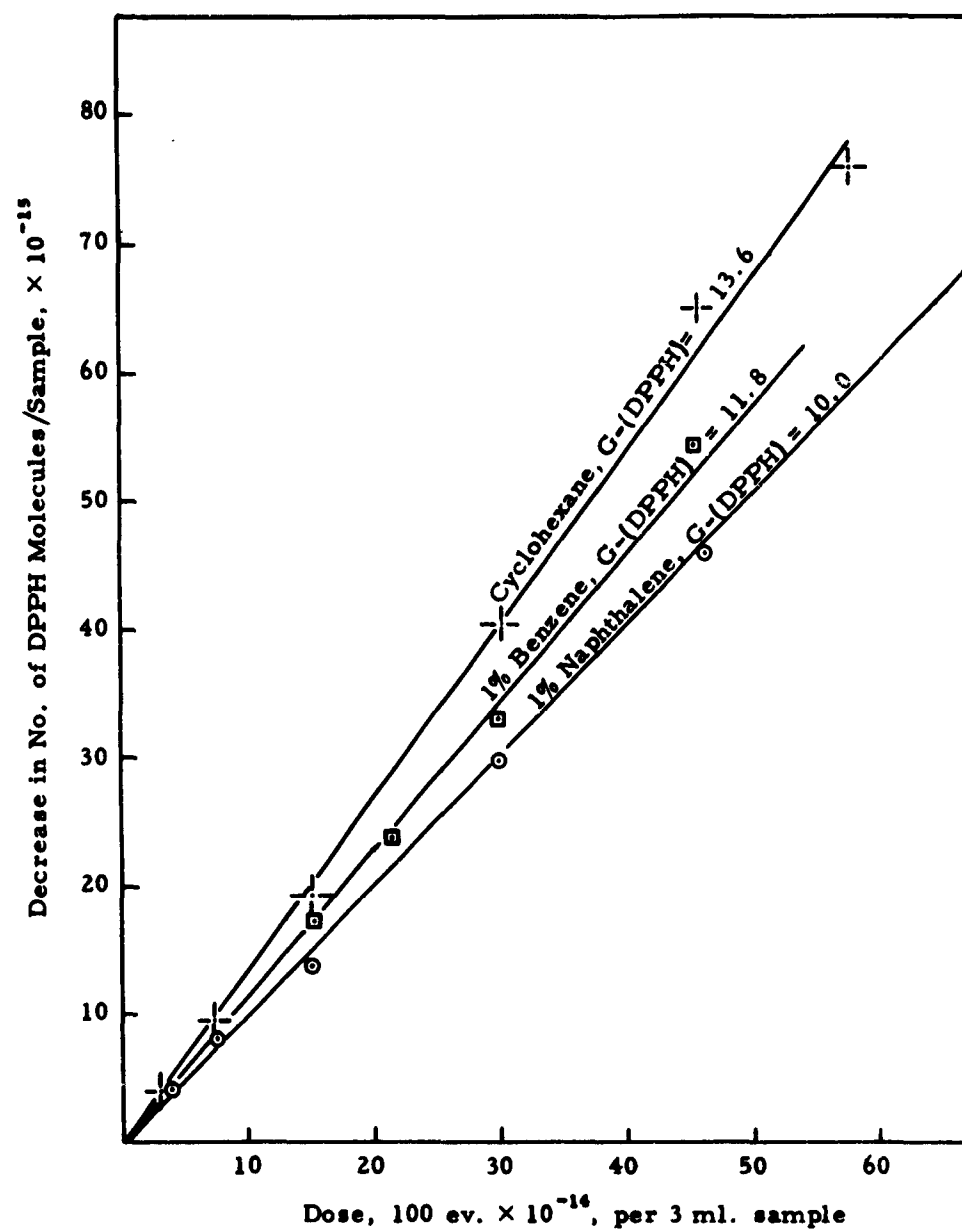


Figure 12. Yield of Free Radicals in Cyclohexane Solutions.

DISCUSSION

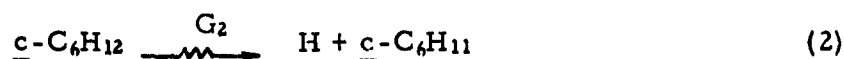
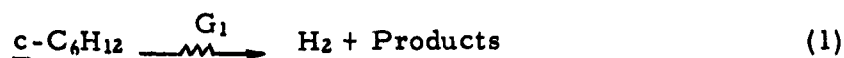
The primary objective of this research was to determine why some compounds are able to protect others from radiolytic degradation. For example, if there were no interaction between the different components of a solution such as cyclohexane and benzene, the cyclohexane product yields would be directly proportional to the fraction of the energy that is absorbed by the cyclohexane. This is not observed. It is assumed that the amount of energy absorbed in a given component is directly proportional to the electron fraction of that component in the system. If the product yields are below this expected "law of averages" value, then some phenomenon other than direct energy absorption and normal degradation processes is occurring.

In order to have a better understanding of the results presented in the previous section and to note more clearly the significance of the pertinent observations, the formation of each product and the effects of additives on its formation will be discussed separately. Then an attempt will be made to integrate all observations into a mechanism that will describe the degradation process.

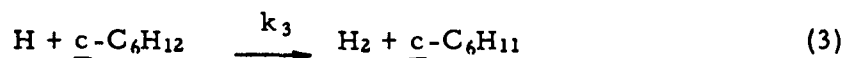
A. HYDROGEN FORMATION

Since there has been much work reported in the literature related to the formation of hydrogen, it was decided that for this research very little emphasis would be placed on repeating this work. It would seem expedient to utilize the results of published work and to relate it to this research or vice versa.

As mentioned earlier, the formation of hydrogen in a pure aliphatic hydrocarbon appears to come from two different reactions. The initiating species for these reactions may be identical or they may be two or even more entities. Hydrogen formation may be represented by the following reactions, using cyclohexane as the hydrocarbon being irradiated.



Assuming that a radical scavenger (S) is present which does not abstract or form hydrogen under the influence of radiation, the following competitive reactions may take place with the hydrogen atoms formed from reaction 2 (H_2 from reaction 1 is assumed not to be influenced by scavengers).



If it is desired to predict $G(\text{H}_2)_s$, ($G(\text{H}_2)$ from the system $\underline{\text{c}}\text{-C}_6\text{H}_{12} + \text{S}$) a steady-state treatment of the above reactions for hydrogen atoms will yield the following equation:

$$\frac{1}{G(\text{H}_2)_o - G(\text{H}_2)_s} = \frac{1}{G_2} \times \frac{k_3}{k_4} \left[\frac{\underline{\text{c}}\text{-C}_6\text{H}_{12}}{\text{S}} \right] + \frac{1}{G_2} \quad (a)$$

$$[G(\text{H}_2)_o] = G_1 + G_2$$

This means that if the hydrogen yield from pure $\underline{\text{c}}\text{-C}_6\text{H}_{12}$ and from $\underline{\text{c}}\text{-C}_6\text{H}_{12} + \text{S}$ is measured, the reciprocal of the difference plotted against the ratio, $[\underline{\text{c}}\text{-C}_6\text{H}_{12}]/[\text{S}]$, gives a straight line with an intercept of $1/G_2$ and a slope of $1/G_2 \times k_3/k_4$. Different scavengers should give the same intercept but the line should have a different slope, which is due to a different k_4 value which in turn is related to the activity of the scavenger (S) and k_4 might have some relation to the disappearance of (S) from solution.

Hardwick^{32, 33} has checked the validity of equation (a) and used it with slight modification to obtain the data from which the relative reactivity values given in Table III were derived. The data of Burton et al.¹⁴ related to the radiolysis of the cyclohexane-iodine system can be plotted according to the above equation to give a straight line. The intercept $1/G_2$ is 0.45 and $G_2 = 2.22$. From these data, an indicated $G_1 = 3.1$ is obtained; $G(\text{H}_2)_o = 5.4$.

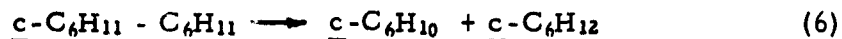
B. CYCLOHEXENE FORMATION

A casual examination of reactions 1 and 2 would suggest that cyclohexene could be derived directly from reaction 1. If reaction 1 is not influenced by any of the products of reaction 2 or by the presence of scavengers, then one would expect the formation of cyclohexene not to be influenced by the presence of additives which react with the products of reaction 2, and the yield of cyclohexene should be almost constant. The yield of cyclohexene is not constant even in the radiolysis of cyclohexane in the absence of additives. This is readily seen from the data of Table V and Figure 2. It has been reported^{8,30} that under prolonged irradiation, the formation of cyclohexene from cyclohexane reaches an equilibrium concentration where $G(\text{cyclohexene}) = 0.6$ and $\Delta G(\text{cyclohexene}) = 0$. At the highest dose shown in Figure 2, it appears that this value has been reached. It is of interest to note that at this dose the presence of benzene, biphenyl, and diphenyl ether has no significant effect on the yield of cyclohexene, whereas at the lower doses these additives significantly reduce the cyclohexene yield. With naphthalene present, the cyclohexene yield is somewhat higher at the high dose and is not greatly reduced at the lower dose.

Since the cyclohexene yield from the radiolysis of pure cyclohexane is reduced with increasing dose, this must be due to the reaction of some of the radiation-formed products with the precursor to cyclohexene. Perhaps cyclohexene itself is reacting with its precursor and is thereby limiting its formation. The fact that the equilibrium concentration of cyclohexene is about the same when additives are present suggests that there is, at lower doses, a competition between the additives and the cyclohexene for reactions with the precursor to the cyclohexene.

These observations suggest that reaction 1 proceeds at a near constant rate, giving a cyclohexene yield of 0.6, while some other reaction proceeds at a varying rate which is dependent upon the concentration of a scavenger. The cyclohexyl radical (from reaction 2) could react with another cyclohexyl radical and through disproportionation form cyclohexene as shown by reactions 5 and 6. The radiation of bicyclohexyl produces some cyclohexane and cyclohexene, which shows that the products of reaction 6 are

formed. This radiolysis has not been studied sufficiently to determine if these products come from a disproportionation reaction or from some other reaction.



If one further examines the data of Tables V, VI, X, and XII and Figures 2 and 3, which are summarized in Table XX, it is seen that the ratio of G(cyclohexene) / G(bicyclohexyl) from the radiolysis of pure cyclohexane (Gi(cyclohexane) = 2.4, Gi(bicyclohexyl) = 2.0) is decreased considerably as the radiation dose is increased. When an additive is present, this ratio gradually increases with increasing dose. Although it is not conclusive, these data indicate that in pure cyclohexane radiolysis, some of the cyclohexene may come from reaction 6; and when an additive such as benzene is present, it is reacting competitively with the cyclohexyl radicals or their precursors.

TABLE XX
THE RATIO OF THE CHANGE IN CYCLOHEXENE AND
BICYCLOHEXYL YIELDS WITH VARYING DOSE

	Dose, 100 ev. $\times 10^{-20}$		
	0.44	1.0	1.66
	$\Delta G(\text{cyclohexene})/\Delta G(\text{bicyclohexyl})$		
Pure cyclohexane	1.76	1.28	1.29
4% Benzene	0.96	1.01	1.21
4% Biphenyl	0.85	0.92	1.02
4% Naphthalene	0.75	0.78	0.85

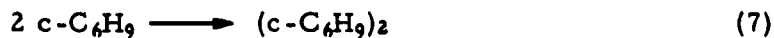
C. BICYCLOHEXYL FORMATION

Bicyclohexyl is one of the major products formed in the radiolysis of cyclohexane. Its initial yield value, G_i , is 2.0. The yield decreases rather rapidly with increasing dose and appears to reach an equilibrium value near 0.6 (Figure 3). When additives such as benzene, biphenyl, or naphthalene are present, the yield of bicyclohexyl decreases very rapidly with increasing additive concentration. The decrease appears to reach a plateau value, however, when the additives are present in quantities greater than about 1% (Figure 5). Bicyclohexyl is undoubtedly formed by a radical combination reaction as in reaction 5, above. The differences in yield values obtained when different additives are present suggest that these additives have varying reactivities. The data plotted in Figure 5 show that naphthalene is most reactive with the cyclohexyl radicals and benzene is the least reactive. Only naphthalene and biphenyl reduce the bicyclohexyl yield to a value less than the equilibrium concentration with no additive present. Apparently the reduction in bicyclohexyl yield is definitely a function of free-radical scavenging by the additive. Aside from the concentration dependency of the yield curves, which indicates scavenging, the identification of phenylcyclohexane in the radiolysis of benzene-cyclohexane solutions, cyclohexyl-naphthalene from naphthalene-cyclohexane solutions and cyclohexylbiphenyl from biphenyl-cyclohexane solutions indicates that these products must be derived from the reaction of the additive with the radiation-produced cyclohexyl radicals. These scavenging reactions are competitive with the radical combination reaction from which bicyclohexyl is formed.

D. BICYCLOHEXADIENE FORMATION

As shown in Figure 4, the various additives reduce the yield of bicyclohexadiene to very low values. These values tend to parallel, but at a much lower yield, the values for cyclohexene. Since the yield of this product is quite low, it probably plays only a minor role in the overall degradation of the cyclohexane. It would be of interest, however, to propose a mechanism for its formation. If the influence of radiation on cyclohexene or its

precursors could result in the formation of cyclohexenyl radicals, then a combination of these radicals as in reaction 7 would form bicyclohexyldiene.



If the cyclohexenyl radical is formed, it could enter into other reactions and presumably be responsible for much of the unsaturation observed in the radiation-produced polymer.

E. PHENYLCYCLOHEXANE FORMATION

The radiolysis of cyclohexane-benzene solutions forms phenylcyclohexane, which is not a product derived from the radiolytic degradation of pure cyclohexane. Figure 7 shows the relation of phenylcyclohexane formation to the formation of other radiolytic products in the radiolysis of solutions containing varying amounts of benzene. Part of these data are plotted on an expanded scale in Figure 8 along with the relation of phenylcyclohexane formation to benzene disappearance. When both G(phenylcyclohexane) and G-(benzene) are calculated and plotted on the basis of energy absorbed by the benzene, it is seen that the yield curves are roughly parallel and that that of G-(benzene) is considerably higher than that of G(phenylcyclohexane), indicating that benzene molecules are entering into reactions other than that of phenylcyclohexane formation. A plot of the change in cyclohexene yield versus the yield of phenylcyclohexane, Figure 13A (data from Table VIII), shows that as the benzene concentration is increased, the rate of decrease in yield of cyclohexene becomes greater (relatively) than the rate of phenylcyclohexane formation. This indicates that benzene is reacting with the precursor to cyclohexene; and since phenylcyclohexane is probably formed via reaction 8, it must be concluded that most of the cyclohexene is formed from some reaction involving cyclohexyl radicals.



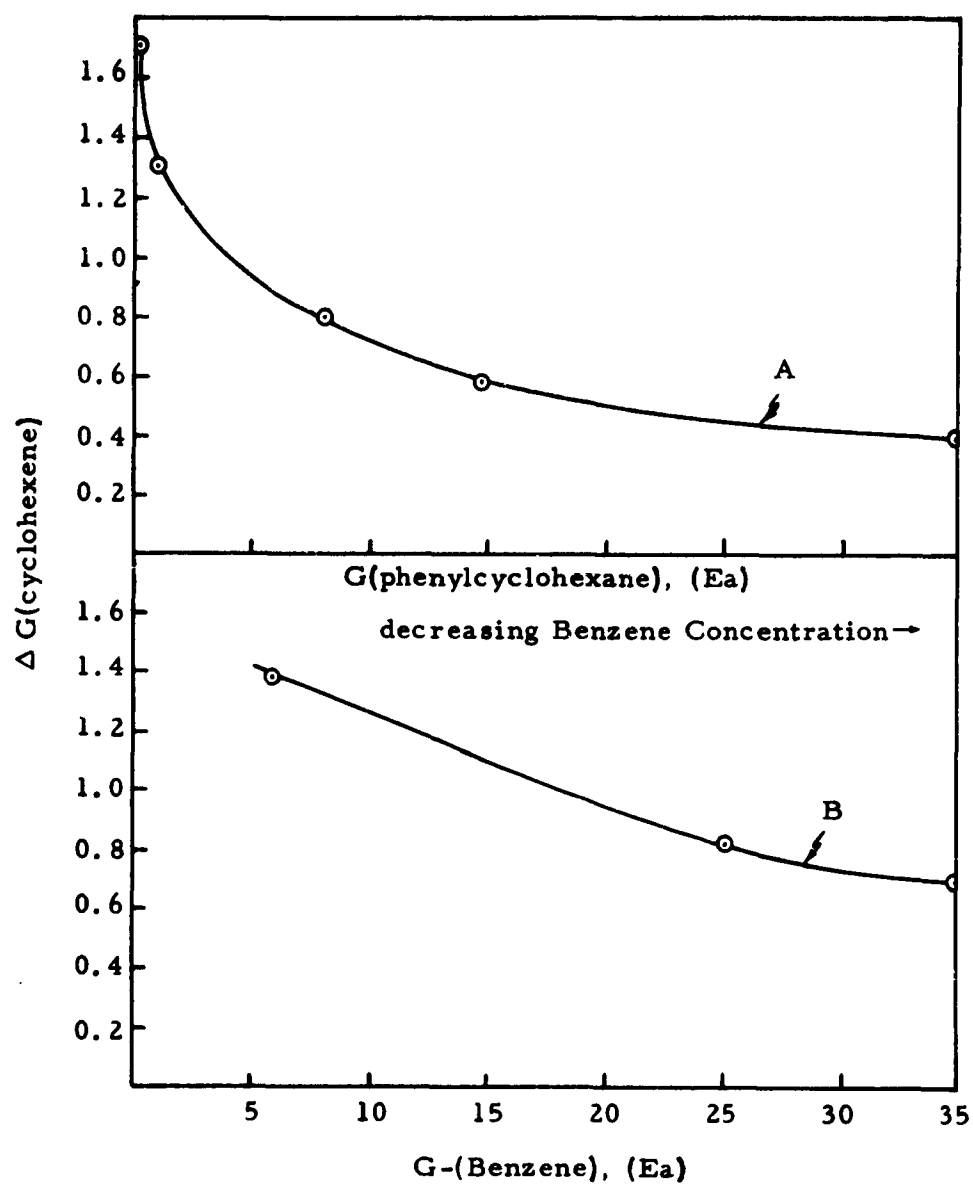


Figure 13. Relation of Change in Cyclohexene Formation to Phenylcyclohexane Formation (A) and to Benzene Disappearance (B) with changing Benzene Concentration.

Figure 13B shows the relation between change in cyclohexene yield and the disappearance of benzene. The linear relationship could indicate that the benzene and the radiolytically formed cyclohexene are in reactive competition for radiation-produced radicals.

The break in the phenylcyclohexane yield curve A, Figure 8, probably indicates the benzene concentration at which optimum scavenging occurs. This concentration is about 5% benzene.

There is insufficient data available to make an analogy between the above statements regarding the cyclohexane-benzene system and the other systems studied. Such an analogy is probably justified, however, since products analogous to phenylcyclohexane have been identified in the other systems studied.

F. ADDITIVE DISAPPEARANCE

As mentioned in the previous paragraphs, when certain aromatic compounds are present in small amounts in cyclohexane during radiolysis, they enter into the degradation reactions and are at least partially consumed by these reactions. The rate of disappearance of benzene, biphenyl, and diphenyl ether appears to be independent of dose at a constant additive concentration. See Figure 6. Naphthalene shows some dependence on dose. The best initial yield values from Figure 6 are shown in Table XXI. For relative reactivity, benzene was given the value of 1.

TABLE XXI
THE INITIAL DISAPPEARANCE VALUES (Gi(A)) AND THE
RELATIVE REACTIVITY OF SOLUTES IN CYCLOHEXANE

Compound	Gi(A)	Relative Reactivity
Benzene	12	1
Diphenyl Ether	5	0.42
Biphenyl	20	1.66
Naphthalene	39	3.25

It is of interest to note that the relative reactivity of these solutes as measured by their disappearance in cyclohexane is quite similar to their reactivity with phenyl radicals produced by the thermal decomposition of benzoylperoxide (see Table I) and to their relative reactivity with hydrogen atoms (Table III). This association of relative reactivity with reactions known to proceed by free-radical mechanisms and the rather large disappearance values for these additives suggest mechanisms more consistent with radical scavenging than with energy transfer. Also in support of free-radical mechanisms is the observation from Figures 3 and 5 which shows that benzene is the least effective and naphthalene is the most effective in reducing the yield of bicyclohexyl. Bicyclohexyl must be formed by a radical combination reaction; and since naphthalene is more reactive toward the cyclohexyl radical than the other additives, it removes more of these radicals from solution before they can combine to form bicyclohexyl. Thus the yield value is lower.

Another point to support free-radical mechanisms as the mode of additive disappearance is the apparent concentration dependency of the G-(additive). From Table VIII and Figure 8, it is seen that G-(benzene) varies from 40 at benzene concentration $E_a = 0.0008$ to G-(benzene) = 3.6 at $E_a = 0.804$. Values of similar magnitude are observed for naphthalene (Table IX) and biphenyl (Table XI).

G. POLYMER FORMATION

Table XXII summarizes the data related to polymer formation from cyclohexane and solutions.

TABLE XXII
DATA FROM POLYMER STUDIES ON IRRADIATED
CYCLOHEXANE SOLUTIONS

	Solution ^a				
	Cyclo- hexane	4% Benzene	4% Bi- phenyl	4% Naphtha- lene	10% Di- phenyl Ether
% Wt. Polymer	2.83	2.80	3.5	4.36	6.1
Molecular Wt.	464	430	440	382	415
G-(polymer) ^b	1.91	2.0	2.5	3.1	4.5
% Additive in polymer ^c	--	34.7-2.8	21.6-15.1	44.6-3.1	37.8-5
G-(additive) ^d	--	11.8	14.1	25.9	7.6
% Additive in polymer ^e	--	24.2	41.0	50.9	35.3
G-(cyclohexane) polymer ^f	--	1.84	1.40	1.39	2.65

^a Dose = 1.66×10^{20} 100 ev. per 2 ml. sample. ^b Total polymer weight converted to molecules of cyclohexane and divided by dose. ^c % additive moiety in polymer as determined by ultraviolet spectroscopy. ^d Additive disappearance calculated on basis of Ea. and GC analysis. ^e % Additive calculated to be in polymer based on d. ^f Total polymer weight minus weight attributed to aromatic moiety converted to molecules of cyclohexane and divided by dose.

The molecular weight of the polymer derived from the radiolysis of pure cyclohexane is higher than that of the other polymers. This is probably due to more definite lower-molecular-weight compounds being formed when an additive is present; e.g., cyclohexylnaphthalenes (mw. = 210) were detected in the polymer derived from the radiolysis of cyclohexane-naphthalene solutions. The method of molecular weight determination biases the final result in favor of the lower-molecular-weight products of a mixture. Based on the molecular weight and the percent phenyl moiety appearing in the polymer derived from the cyclohexane-benzene solution, calculations show that the "average polymer molecule" would contain two phenyl groups and about 3.5 cyclohexyl groups; the pure cyclohexane "average polymer molecule" would consist of about 5.6 cyclohexyl groups. The biphenyl polymer would contain an average of 3.5 cyclohexyl groups per biphenyl group and the naphthalene polymer would consist of 1.5 naphthalene units for each 2 cyclohexyl groups. These figures all indicate that the additive is capable of reacting, and probably does react, with more than one cyclohexyl radical in the formation of polymer.

The data of Table XXII are primarily significant in showing that an aromatic solute composes a rather large portion of the polymer. This has been shown by two methods of analyses and calculations. Further, the data show that an additive molecule can react with more than one cyclohexyl radical. By eliminating from the total polymer the contribution of the additive and recalculating the polymer yield in terms of cyclohexane molecules only converted to polymer, the presence of additives reduces, slightly, the amount of cyclohexane consumed in polymer formation. (Diphenyl ether seems to be unusual in this respect; however, this might result from cleavage of the ether molecule and will not be considered further.)

Cyclohexane-benzene (liquid state) irradiations at a lower dose and with varying benzene concentrations (see Table XIV) show a tendency toward a decrease in polymer yield with decreasing benzene concentration. The influence of additives capable of scavenging cyclohexyl radicals has little or no effect on the yield of cyclohexane converted to polymer.

H. THE INFLUENCE OF SOLID-STATE IRRADIATIONS

A comparison of yield values derived from the liquid- and solid-state radiolysis of cyclohexane-benzene solutions is shown in Table XIV. Solid-state radiolysis reduces the yield of "pre-cyclohexane" products, cyclohexene, bicyclohexyldiene, phenylcyclohexane, and polymer. These reductions suggest that the mode of formation of these products is dependent upon a migration of the precursor from the site of formation; i. e., the reactions are diffusion controlled. The solid state slows down the process of diffusion but does not stop it completely. The yield of bicyclohexyl is greatly increased in the solid-state irradiation. If freedom of migration is reduced in the solid state and several cyclohexyl radicals are formed in the environment of a radiation track, they have a greater probability of combining than they would if a state of free diffusion existed.

The solid-state-irradiation naphthalene and biphenyl solutions show the same trend in yield product formation (Table XV and XVI). In these irradiations, the disappearance of additive was determined and was found to be very significantly reduced by solid-state irradiation, which very strongly suggests free-radical diffusion controlled mechanisms.

I. FREE-RADICAL SCAVENGING

In the previous sections there has been much indication that free-radical mechanisms are responsible for the greatest part of the radiolytic degradation of cyclohexane and that much of the effect of aromatic additives is due to their scavenging of the radiation-produced radicals. Diphenylpicrylhydrazyl (DPPH) has been used as a scavenger to measure the rate of radical formation in various systems. DPPH is much more reactive toward free radicals and particularly hydrogen atoms than many of the aromatic compounds (see Table III). If it can be assumed that in dilute solution DPPH scavenges most of the free radicals formed during a radiolysis, then a comparison of the free-radical yields derived from DPPH radical counting methods with those obtained by using additives such as benzene should indicate

the efficiency of the additive for reaction with the radicals. Tables XVII, XVIII, and XIX show the analytical data obtained from irradiating cyclohexane-DPPH and cyclohexane-DPPH-benzene solutions. The $G(\text{DPPH})$ values are equal to the rate of free-radical formation, $G(R)$. These data are plotted in Figures 9-12 and show graphically that the disappearance of DPPH varies slightly and is somewhat dependent upon the original DPPH concentration. Curves A and B of Figure 9 have been replotted in Figure 11, Curves A and B. The slope of these curves is equivalent to the "extrapolated-to-zero-dose" value, $G_i(\text{DPPH})$. For the $2.56 \times 10^{-5} \text{ M}$ DPPH, $G_i(R) = 18.0$; and for the $5.112 \times 10^{-5} \text{ M}$ DPPH solution, $G_i(R) = 16.25$. Figure 10 and curves C-F of Figure 11 show the effects of adding small amounts of benzene to the cyclohexane-DPPH solutions. It is seen that the rate of disappearance of DPPH is reduced by the presence of benzene and that the amount of reduction is dependent upon the concentration of the benzene. This reduction does not represent a reduction in the rate of free-radical formation but is due to a competition of the DPPH and benzene for reaction with the cyclohexyl radicals or hydrogen atoms. One might argue that the reduction is due to fewer radicals being formed as the result of energy transfer processes. This argument, however, is not valid since it has been shown that there is a slight decrease in benzene concentration during the irradiation. Due to the extremely low doses, it is impossible (by ultraviolet and infrared spectroscopic techniques) to assign a quantitative value to this disappearance. Enough measurements were made to establish that benzene is consumed by the reaction. Further evidence to indicate that the reduction in DPPH disappearance with another additive present is the result of competitive radical scavenging reactions rather than energy transfer phenomena is shown in Figure 12. In previous sections, it was shown that the relative reactivity of naphthalene is considerably higher than benzene for reaction with radicals. If the reduction in rate of DPPH disappearance with another additive (benzene) present is due to competition, the presence of naphthalene should further reduce the rate of DPPH disappearance. This is shown to be true in Figure 12. The values in this figure were obtained from 1% by weight of benzene and naphthalene in the cyclohexane-DPPH solution. The increased activity of the naphthalene over that of the

benzene should actually be about 1.7 fold greater than is indicated in Figure 12, since in these solutions the number of benzene molecules present is about 1.7 times that of the naphthalene molecules and any reactions of this type would be dependent upon numbers of molecules rather than weight values.

Several attempts were made to determine whether the presence of DPPH had any effect on the formation of hydrogen. Since the total dose required to maintain a detectable quantity of DPPH is very low, there was not enough hydrogen formed to make analysis reliable. Based on the work done, however, it seems likely that DPPH has little effect on the formation of hydrogen.

PROPOSED MECHANISMS AND CONCLUSIONS

This study is concerned with identifying the products and determining the rates of product formation in the radiolysis of cyclohexane and cyclohexane containing aromatic solutes. The experimental data consist of physical and chemical facts which must be considered in postulating a mechanism for the mode of radiolytic degradation. These are summarized below.

a. Cyclohexene has an initial yield value (G_i) of 2.4. Under prolonged irradiation, the formation of cyclohexene reaches an equilibrium concentration at which $G(\text{cyclohexene}) = 0.6$. The presence of aromatic additives is effective in reducing the $G_i(\text{cyclohexene})$ but does not reduce significantly the equilibrium concentration value.

b. Bicyclohexyl has an initial yield value (G_i) of 2.0 and approaches an equilibrium concentration at which $G(\text{bicyclohexyl}) = 0.6$. At high doses, the rate of bicyclohexyl formation is the same as the rate of cyclohexene formation. At lower doses, the change in rate of cyclohexene formation is greater than that of bicyclohexyl. Additives reduce the rate of bicyclohexyl formation at a much faster rate than that of cyclohexene. Different additives exert differing rate-decreasing effects on the formation of bicyclohexyl, whereas in the formation of cyclohexene these effects are not so great.

c. Aromatic additives present in cyclohexane during radiolysis disappear from the solution at a rate faster than would be predicted from the law of averages, and the rate of disappearance is quite characteristic of the additive. Some of the reacted additive appears in definite compounds, e. g., phenylcyclohexane when benzene is the additive, and the remainder is found in the polymer where it appears that the additive has been polysubstituted. The rate of additive disappearance is almost independent of radiation dose but is somewhat dependent upon the initial additive concentration.

d. The presence of aromatic additives increases the rate of total polymer formation. In terms of cyclohexane converted to

polymer, the polymer yield decreases slightly with additive present. Although not dramatically indicated, this rate of decrease appears to be somewhat related to the relative reactivity of the additive. The general decrease in molecular weight of the polymer with increasing reactivity of the additive is attributed to the formation of greater quantities of definite compounds involving the additive.

e. The yield of cyclohexene, bicyclohexyldiene, phenylcyclohexane, and polymer from cyclohexane-benzene solutions is significantly reduced in solid-state irradiations as compared to irradiation in the liquid state. Similar reductions are observed with other additives. Also, the additive disappearance rate is decreased while the yield of bicyclohexyl is greatly increased.

f. The rate of free-radical formation as measured by the disappearance of diphenylpicrylhydrazyl (DPPH) is slightly dependent upon the initial DPPH concentration. The initial yield (G_i) of free radicals is shown to range between 16.25 and 18.0. Irradiation of cyclohexane-DPPH solutions with benzene present reduces the rate of DPPH disappearance. The amount of reduction is a function of the benzene concentration. Naphthalene, in equivalent molar concentration, is more effective than benzene in reducing the rate of DPPH disappearance. In these reactions, it must be assumed that the presence of the additives does not affect the rate of radical production from the cyclohexane. Accepting this assumption, it must be concluded that the benzene and naphthalene are reacting competitively with the DPPH. The data in Figure 12 show that naphthalene is about five times more reactive than benzene in competing with DPPH in the radical scavenging reactions. This compares favorably with the relative reactivity of these solutes as determined by other methods (Table III and XXI).

g. The product yield results for the radiolysis of pure cyclohexane are summarized in Table XXIII.

TABLE XXIII
INITIAL YIELD VALUES (Gi) OF PRODUCTS FORMED
IN THE IRRADIATION OF PURE CYCLOHEXANE

Product	Gi	
Hydrogen	5.5 ^a	
Cyclohexene	2.4	Hydrogen equivalent = 5.8
Bicyclohexyl	2.0	
Bicyclohexadiene	0.2	
Polymer ^b	2.0	
^a Literature value.	^b Estimated value.	

The hydrogen balance is excellent if one considers the uncertainty of the initial yield of polymer. If one assumed that $G_i(\text{polymer}) = 0$, the hydrogen equivalent would be 4.8, which is quite low. It would be reasonable to postulate that the $G_i(\text{polymer}) \leq 2$. Most significant, however, is the indication that in order to achieve a reasonable hydrogen balance, the $G_i(\text{polymer})$ must be greater than zero, thus inferring that polymer formation occurs simultaneously with the formation of the other yield products.

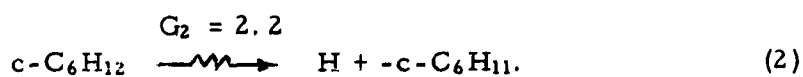
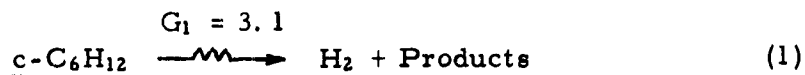
h. Table XXIV summarizes the initial product yield values for the radiolysis of cyclohexane with 4% benzene.

TABLE XXIV
INITIAL YIELD VALUES (Gi) OF PRODUCTS FORMED IN
THE IRRADIATION OF CYCLOHEXANE WITH 4% BENZENE

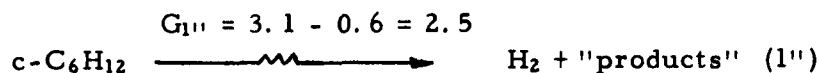
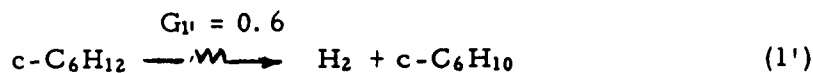
Product	Gi	
Hydrogen	3.2 ^a	
Cyclohexane	1.4	
Bicyclohexyl	0.8	Hydrogen equivalent = 4.1
Bicyclohexadiene	0.04	
Phenylcyclohexane	0.3	
Polymer ^b	1.8	
^a From Figure 1.	^b Estimated value.	

These results indicate the same conclusions regarding polymer formation as were made above.

From the literature, the most probable reactions leading to the formation of hydrogen are



One would like to suggest that the "product" of reaction 1 is cyclohexene which would give a cyclohexene yield of 3.1, which is not observed. Prolonged irradiation or the presence of additives capable of radical scavenging does not reduce the yield of cyclohexene below 0.6, which suggests that reaction 1 proceeds via two routes as indicated below.



Barker and Hill⁵ observed that the formation of polymer reaches a steady state and maximum yield value of 2.5. If these polymer yield values are plotted against the yield of cyclohexene with varying dose (see Figure 14), the two curves are almost complementary, which would indicate a definite relationship between cyclohexene formation and polymer formation and reaction 1'' must be associated with both. Since the formation of polymer is undoubtedly via free-radical reactions, it is, therefore, presumed that reaction 1'' can yield cyclohexene and hydrogen as well as polymer via a free-radical mechanism. A proposed reaction sequence (I) for this is shown below.

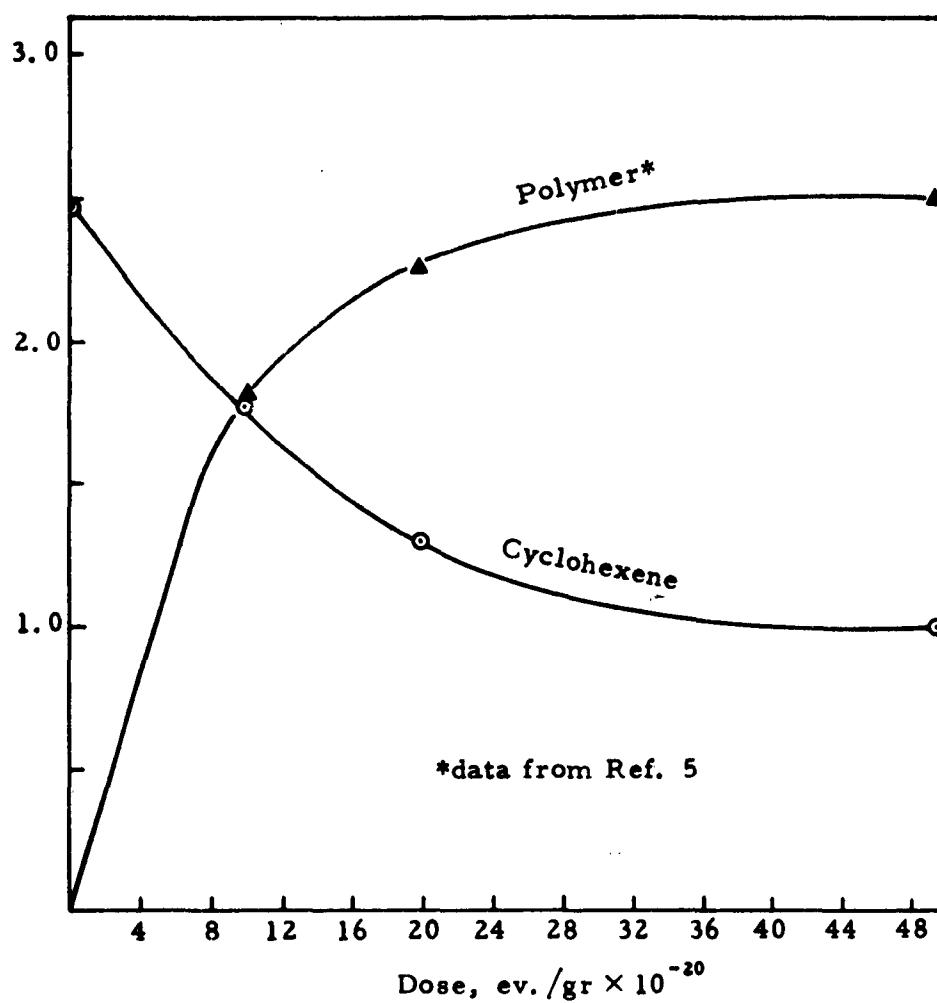
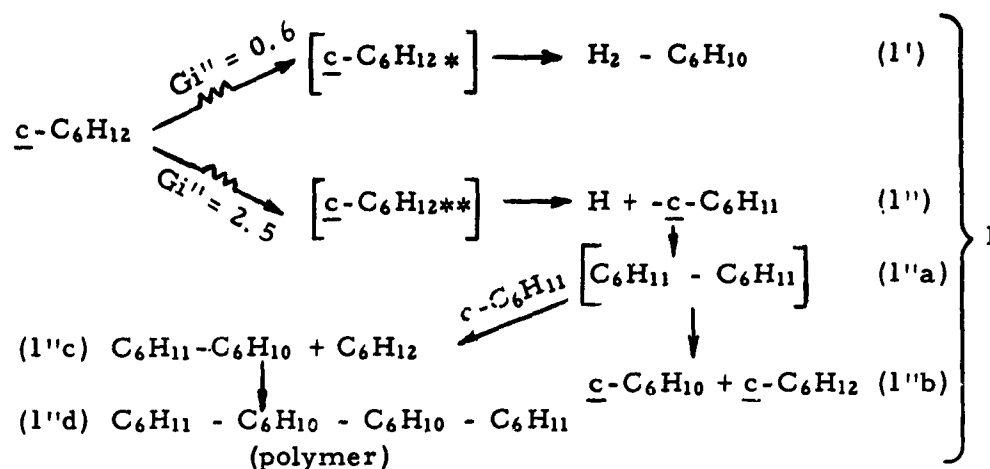


Figure 14. Relation of Cyclohexene Formation to Polymer Formation.



If this reaction sequence is to explain the experimental observations, then, in order to have a decreasing yield of cyclohexene while the yield of polymer increases, something must happen to the bicyclohexyl species in reaction 1''a. This bicyclohexyl species could very well be formed in an excited state which possesses enough energy to allow the disproportionation reaction 1''b to occur. When radiation-produced products accumulate, these may permit sufficient transfer of energy from the excited state to make reaction 1''b no longer possible, and then reaction 1''c predominates. The free radical, $\text{C}_6\text{H}_{11} - \text{C}_6\text{H}_{10}$, can then combine with another radical to form polymeric products.

The experimental evidence to support the above mechanisms, aside from the relation of cyclohexene formation to polymer formation, is derived from the effect of benzene on the rate of cyclohexene formation, phenylcyclohexane formation, and polymer formation. As the benzene concentration is increased, the rate of decrease in yield of cyclohexene becomes greater than the rate of phenylcyclohexane formation. Thus, if the benzene was reacting solely with the $\text{c-C}_6\text{H}_{11}$ radical of reaction 1'', one would expect a reduction in cyclohexene yield equivalent to the yield of phenylcyclohexane formation. This is not observed. The benzene must be preventing reaction 1''b from occurring by changing the mode of reaction of the proposed excited state of bicyclohexyl. This could most readily be done by a transfer of energy as suggested in the previous paragraph. Also, since the rate of cyclohexane converted to polymer is not greatly reduced

by the presence of benzene, it indicates that the rate of reaction 1''c is not changed significantly.

If the hydrogen produced by reaction 1 was produced entirely by a molecular process, one would expect very little or no reduction in hydrogen yield from this reaction when a scavenger is present. This is not observed. Burton et al.¹⁴ reported a residual hydrogen yield value of 0.5 that is not scavenged by iodine. This value corresponds to the yields of reaction 1'.

The formation of bicyclohexyl is undoubtedly the result of a radical combination reaction as indicated by reaction 3.



The origin of the cyclohexyl radicals for this reaction is not definite. Perhaps bicyclohexyl is formed primarily from the combination of radicals produced in reaction 2. Scavenger additives are quite effective in reducing the yield of bicyclohexyl. If bicyclohexyl was predominantly formed through reaction 1''a, one would expect a relation between the yield of bicyclohexyl and the yield of cyclohexene and/or polymer. Such a relation does exist; however, as shown in Figure 3, different additives have different effects on the equilibrium yield value of the bicyclohexyl, which is attributed to the relative reactivity of the scavenger.

A summation of the total yield of free radicals expected from reactions 1'' and 2 would give a value of 18.8 (Table XXV).

TABLE XXV
EXPECTED YIELD OF RADICALS FROM THE
RADIOLYSIS OF CYCLOHEXANE

Reaction	Radical	Yield
1''	H	5.0
1''	c-C ₆ H ₁₁	5.0
2	H	4.4
2	c-C ₆ H ₁₁	4.4

The maximum value for the yield of free radicals from pure cyclohexane as measured by DPPH is 18.0, which is in excellent agreement with the expected value. The addition of additives such as benzene or naphthalene to the cyclohexane-DPPH solutions reduces the "apparent" yield of free radicals. This "apparent" reduction is attributed to a competition between the DPPH and the additive for reaction with the free radicals formed. Proof that DPPH and benzene are reacting competitively would lie in establishing a free-radical yield balance. Using an approximation of $G(H_2) = 4$ from Figure 1 and the product yield values from Column 9, Table VIII for a near 1% benzene in cyclohexane solution, the figures in Table XXVI are derived.

TABLE XXVI
CONSUMPTION OF RADICALS TO FORM PRODUCTS IN THE
RADIOLYSIS OF CYCLOHEXANE-BENZENE SOLUTION

Component	G	G Radical Equivalent
Hydrogen	4	8
Cyclohexene	1.26	2.52
Bicyclohexyl	0.81	1.62
Phenylcyclohexane	0.14	0.14
Polymer	2	<u>2</u>
Total		14.28

These data indicate that a total of 14.3 radicals per 100 ev. were consumed to form the major yield products. This represents a reduction of 20.5% from the value expected if benzene was not entering into any of the reactions. The data plotted in Figure 12 indicate that benzene reduces the radical yield value by 13.2%. These values are in good agreement when differences in dose and dose rate are considered. It therefore must be concluded that an additive such as benzene is entering into the radiolytic reactions of cyclohexane via free-radical mechanisms. The "apparent" reduction in radical yield from these data is $18 - 14.3 = 3.7$. This value should represent the extent to which benzene has reacted during the radiolysis. Assuming that one benzene molecule reacts with an average of 1.75 cyclohexyl

radicals (see section V, G), then $3.7/1.75 = 2.1$ plus the yield of phenylcyclohexane (0.14) = 2.24 should be the expected disappearance value for benzene. This compares quite favorably with the value of 2.9 (Table VIII) obtained by gas chromatography.

Examination of the data related to solid-state irradiations shows that the major products (cyclohexene and polymer) associated with reaction 1'' are reduced when compared to liquid-state irradiations. The formation of bicyclohexyl, which is indicated by reaction 2, is increased very significantly by solid-state irradiation. The primary significance of these observations is the indication that reactions associated with the radicals formed from reaction 2 are controlled less by diffusion processes than are the reactions associated with reaction 1''. This is to say that the formation of reaction 1'' products is dependent upon the migration of the reactive species from the environment of its formation. Where the freedom of migration is reduced, as in the solid state, the yield of these products is reduced.

All of these data tend to support the reaction sequence I. The following conclusions can be made.

- a. At least two and probably three activated cyclohexane species are initially formed during the radiation degradation process. These are the [\underline{C} -C₆H₁₂*] from reaction 1', which formed a small amount of molecular hydrogen and some cyclohexene; the [\underline{C} -C₆H₁₂**] (reaction 1''), which decomposes into atomic hydrogen and the cyclohexyl radical; and possibly a third species, which decomposes into the cyclohexyl radical of reaction 3. The [\underline{C} -C₆H₁₂**] and [\underline{C} -C₆H₁₂***] may be identical or they may differ only by a state of energy.
- b. The only products which appear not to be derived from free-radical reactions are hydrogen and cyclohexene from reaction 1', and this accounts for only a minor amount of the initially formed products.
- c. The major part of the hydrogen and cyclohexene plus all of the other products are formed directly by free-radical processes. The only point in the reaction sequence where energy transfer may play a role is in the disproportionation reaction 1''b;

and here it is only conjecture, since nothing is known regarding the relative energies required to make reaction 1''b take precedence over reaction 1''c.

d. Additives such as benzene, biphenyl, naphthalene, and presumably diphenylpicrylhydrazyl exert their influence on the radiolytic degradation of cyclohexane almost exclusively by free-radical scavenging reactions. Benzene, biphenyl, and naphthalene are capable of reacting competitively with the normal reactants, thereby removing many of the radiation-produced radicals and thus affecting the observed reduction in yield of products derived from the radiolysis of cyclohexane. Each molecule of these additives is capable of reacting with more than one radiation-produced radical, and most of the resulting products appear in the polymer residue.

e. Solid-state irradiation results compared to those of the liquid state fully support the free-radical mode of degradation.

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APPENDIX
DEFINITION OF TERMS COMMONLY USED IN
RADIATION CHEMISTRY

1. Electron-volt, ev. - Energy acquired by any charged particle carrying unit electronic charge when it falls through a potential difference of one volt. This energy unit represents 1.6021×10^{-12} ergs.
2. G value or yield value is the term used to designate the number of molecules of a substance being formed or destroyed for each 100 ev. of energy absorbed during irradiation. As an example, $G(x) = 1$ means that one molecule of substance x is formed for each 100 ev. of energy absorbed; $G-(x)$ means the destruction of substance x. $G_i(x)$ is the extrapolated-to-zero-dose yield value for substance x, i. e., the initial yield value.
3. Dose is the measure of the energy, usually expressed in ev. or 100 ev. units, absorbed by the system.
4. Dose rate is the measure of energy absorbed by the system per unit of time.
5. Dosimetry is the method by which dose rate is determined. This can include calorimetry, ionization methods, direct calculation, charge collection, and various chemical methods.
6. Extranuclear electrons are the electrons of an element generally considered to be its valence electrons. Energy absorption by a compound is generally considered to be proportional to the number of extranuclear electrons present in the medium.
7. Electron fraction is the number of extranuclear electrons in compound x in the mixture divided by the total number of extranuclear electrons in the mixture. As an example, a benzene molecule has 42 extranuclear electrons; cyclohexane, 48. A 1:1 weight solution of benzene and cyclohexane can be calculated in electron fraction cyclohexane as follows:

$$E_{\text{cyclohexane}} = \frac{1/84 \times 48}{1/84 \times 48 + 1/78 \times 42} = 0.515$$

where 84 and 78 = molecular weight of cyclohexane and benzene respectively.

In the above solution, the cyclohexane can be considered to absorb 51.5% of the total energy received by the solution.

In this work, E_a designates the electron fraction of additive in cyclohexane.

8. Activated species is generally considered to be a molecule which has received sufficient energy to initiate its degradation process. This species cannot be detected by chemical means, and its presence can be inferred only by its subsequent reactions.

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